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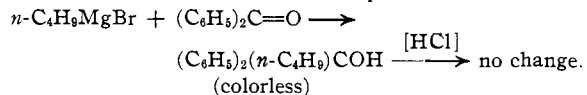
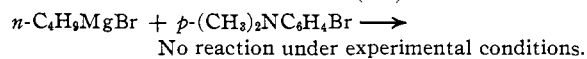
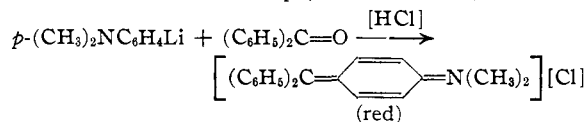
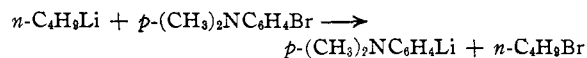
Color Tests for Some Organolithium Compounds

BY HENRY GILMAN AND JACK SWISS*

A sensitive, qualitative color test for moderately and highly reactive organometallic compounds has been available for a number of years.¹ In recent work concerned with the preparation of Grignard reagents from organolithium compounds and the preparation of aryllithium compounds from alkylolithium compounds, a need was felt for more selective color tests: one which might differentiate between a Grignard reagent and the corresponding organolithium compound; and another to differentiate between an alkylolithium compound and an aryllithium compound.

Two such tests are proposed here, the first (Test A) depending upon the greater reactivity of alkylolithium compounds over aryllithium compounds and organomagnesium compounds in halogen-metal interconversion reactions; and the second (Test B) depending upon the fact that triphenylmethylolithium is colored and triphenylmethylmagnesium halides are not formed under the conditions of the experiment.

In both tests the procedure is quite simple. In Test A, one-half to one cc. of the organometallic solution is added to an equal volume of a 15% solution of *p*-bromodimethylaniline in dry benzene. Then one cc. of a 15% solution of benzophenone in dry benzene is added, and after a few seconds the mixture is hydrolyzed with water and acidified with concentrated hydrochloric acid. A red color in the water layer is a positive test for a "reactive" organolithium compound. The reactions involved with *n*-butyllithium and with *n*-butylmagnesium bromide are as follows:



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(1) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925). The most recent study concerned with this color test is by Gilman and Jones, *ibid.*, **62**, 1243 (1940).

Limitations of Test A are described in the Experimental Part.

Test B is carried out by adding one to two cc. of the organometallic mixture to one-half cc. of a saturated solution of triphenylmethane in benzene or ether. Those organolithium compounds which will metalate triphenylmethane laterally give a characteristic yellow color within one-half to two minutes. With Grignard reagents no color is observed.

Both tests are slightly less sensitive than the Michler ketone test, but are of the same order of sensitivity. With *n*-butyllithium, using one cc. of test solution, the lowest concentration which will give a positive test lies between 0.02 and 0.03 molar.

Incidentally, the prompt conversion of organolithium compounds to the corresponding Grignard reagents by means of magnesium bromide or iodide is of some preparative value for the synthesis of Grignard reagents otherwise obtained with difficulty. For example *p*-dimethylaminophenylmagnesium bromide is prepared from the halide with difficulty and in poor yields, whereas *p*-dimethylaminophenyllithium is obtainable in 96% yield.² The latter compound is readily converted to the corresponding RMgX compound by magnesium iodide.³ The reaction may also prove of value in converting some readily accessible mono- and poly-organosodium and organopotassium compounds to the corresponding RLi and RMgX types.

Experimental Part

Test A (*p*-Bromodimethylaniline, Benzophenone and Hydrochloric Acid).—One cc. of a 0.1 *M* solution of *n*-butyllithium gave a deep red color; 1 cc. of a 0.03 *M* solution gave a red color; and 1 cc. of a 0.02 *M* solution gave no color (but did give a faintly positive color in the Michler ketone test¹). One-half cc. of a 1.0 *M* solution of *n*-butyllithium in petroleum ether (b. p., 28–38°) gave a deep red color. One cc. of a 0.1 *M* solution of triphenylmethylolithium gave a deep red color; in this test the yellow color of triphenylmethylolithium was discharged immediately when the *p*-bromodimethylaniline was added. One cc. of 0.8 *M* phenyllithium gave an orange color; in this test a deep red color was observed when the phenyllithium was al-

(2) Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

(3) Unpublished studies by R. H. Kirby on reactions of different RM compounds with some conjugated systems.

lowed to react for one minute with the *p*-bromodimethylaniline before adding the benzophenone. Methylithium (2 cc., 0.6 *M*) gave no color and 5 cc. of 0.6 *M* phenylethynyllithium gave no color. A suspension of benzylsodium in toluene (0.25 cc., 1.5 molar) gave a red color.

Mr. C. G. Stuckwisch observed no color when one cc. of 4-dibenzofuryllithium (0.15 *M*), 4-dibenzothieryllithium (0.32 *M*) and 4-lithio-*N*-ethylcarbazole (0.18 *M*) were treated under Test A conditions. Each of these gave, of course, the Michler ketone test. No color was observed with 9-fluorenyllithium (1 cc., 0.5 *M*).

No color was observed with ethylmagnesium bromide (1 cc., 2 *M*), *n*-butylmagnesium bromide (2 cc., 1 *M*), phenylmagnesium bromide (2 cc., 1 *M*), [*n*-butyllithium + MgI₂] (1 cc., 0.2 *M*), and [triphenylmethylithium + MgI₂] (1 cc., 0.2 *M*). Of these five tests, a transient red color was noted as the benzophenone solution was added to ethyl- and *n*-butylmagnesium bromides, but this color disappeared upon hydrolysis.

o-Bromodimethylaniline and *m*-bromodimethylaniline are not so satisfactory as *p*-bromodimethylaniline since the colors formed with them are less intense. One cc. of a one molar solution of *n*-butyllithium in petroleum ether gave a lemon yellow color with *o*-bromodimethylaniline, an orange color with *m*-bromodimethylaniline and a deep red color with *p*-bromodimethylaniline. By using a compound which will undergo halogen-metal interconversion more readily, for example, 3-methoxy-4-bromodimethylaniline instead of *p*-bromodimethylaniline, it should be possible to extend the test to include the less "reactive" organolithium compounds, the term "reactive" being used here in the sense of reactivity in halogen-metal interconversions.

Some Limitations of Test A.—Test A should respond to all RM compounds that can effect a fairly prompt halogen-metal interconversion with *p*-bromodimethylaniline. RM compounds of generally lesser reactivity⁴ than the organolithium compounds, such as the Grignard reagent and organoaluminum compounds, effect halogen-metal interconversions very slowly and so should give no positive test under the experimental conditions designated. There are, however, significant differences among the RLi compounds. As mentioned in a preceding paper,⁵ the order of decreasing effectiveness of some RLi compounds in the halogen-metal interconversion reaction with α -bromonaphthalene is: *n*-propyl, ethyl, butyl, phenyl and methyl. In general, it now appears that all alkylithium compounds with the exception of methylithium and the ethynyllithium compounds like phenylethynyllithium will give positive results with Test A. On the other hand, the aryllithium compounds generally will react so slowly that a differentiation can be expected between them and the alkylithium compounds (see experimental data). This difference in reactivity makes it generally possible, by means of Test A, to determine when *n*-butyllithium is no longer present in metalation reactions.

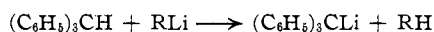
Test B (Triphenylmethane).—One cc. of a 0.1 *M* solution of *n*-butyllithium gave a yellow color in ten seconds; and 3 cc. of a 0.03 *M* solution gave a yellow color in thirty

seconds. One-half cc. of one molar *n*-butyllithium in petroleum ether (b. p. 28–38°) gave an immediate yellow color; and 1 cc. of this solution gave an immediate orange-yellow color when added to a solution of fluorene in ether. It is quite probable that other triarylmethanes or related types may give more pronounced colors. One cc. of 0.8 *M* phenyllithium gave a yellow color in thirty seconds with triphenylmethane.

No color was observed with 2 cc. of 0.15 molar 4-dibenzofuryllithium in ten minutes, 2 cc. of 0.6 molar methylithium in ten minutes, 2 cc. of one molar *n*-butyl- or phenylmagnesium bromide in ten minutes, and a mixture of triphenylmethylithium and magnesium iodide. In this last test the color of triphenylmethylithium was discharged on the addition of magnesium iodide, but the solution still gave a strong Michler ketone test, showing that the Grignard reagent had been formed. One cc. of methylithium (0.6 molar) gave an immediate yellow color with fluorene in ether; with triphenylmethane a color developed after one hour.

In order to determine whether triphenylmethane is metalated laterally by *n*-butylmagnesium bromide, 0.02 mole of the former was refluxed for two hours with 0.05 mole of the latter in 100 cc. of 1:1 ether-benzene. Upon carbonation there was obtained only valeric acid and no trace of triphenylacetic acid.

Some Limitations of Test B.—Test B should respond, in general, to the organometallic compounds of potassium, sodium and lithium. Inasmuch as the test is concerned primarily with relative acidities



it follows that if the RLi compound is derived from an acid (RH) which is much stronger than the "acidic" or active lateral hydrogen in triphenylmethane, there will be no replacement of the hydrogen in triphenylmethane by lithium. This would mean, for example, that phenylethynyllithium would give no color test because phenylacetylene is a stronger acid than triphenylmethane.⁶ The anomalous behavior of methylithium with triphenylmethane has its parallel in other metalation reactions, for example, in the metalation of dibenzofuran.⁷

No Grignard reagent should give Test B, not only because dilute solutions of triphenylmethylmagnesium halides are colorless, but also because it has been shown⁸ that at least some RMgX compounds do not react with triphenylmethane. A 0.3 molar solution of triphenylmethylithium has a deep red color; corresponding solutions of triphenylmethylmagnesium bromide and iodide are orange-yellow.

Miscellany.—Two cc. of an ether suspension of triphenylmethylithium (prepared from triphenylchloromethane and lithium amalgam⁹) was added to an ether solution of *p*-bromodimethylaniline. To the resulting mixture was then added benzophenone, and after hydrolysis the aqueous solution gave a bright red color when made strongly acid with concentrated hydrochloric acid.

(4) See pp. 435–439 of Gilman "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938.

(5) Gilman and Moore, *THIS JOURNAL*, **62**, 1843 (1940). See Gilman and Banner, *ibid.*, **62**, 344 (1940), for the halogen-metal interconversions with *m*- and *p*-bromodimethylanilines.

(6) Conant and Wheland, *ibid.*, **54**, 1212 (1932); McEwen, *ibid.*, **58**, 1124 (1936).

(7) Unpublished studies by Mr. H. B. Willis.

(8) See, also, Gilman and Leermakers, *Rec. trav. chim.*, **48**, 577 (1929).

(9) Grosse, *Ber.*, **59**, 2652 (1926).

An equimolecular mixture of *n*-butyllithium and phenylmagnesium bromide gave a positive color test with Michler ketone, but no test with *p*-bromodimethylaniline.

A 25-cc. aliquot of a 75-cc. ether solution containing 0.05 mole of *n*-butyllithium was shaken for one minute with 5 cc. of α -bromonaphthalene and there was obtained, subsequent to carbonation, 2.55 g. (87%) of α -naphthoic acid. To the remainder of the solution was added in one portion 0.05 mole of magnesium iodide in 100 cc. of ether. Vigorous refluxing occurred for a few seconds. After stirring for one and one-half minutes, a 25-cc. aliquot was withdrawn, treated for one minute with 5 cc. of α -bromonaphthalene in 25 cc. of ether and then the mixture was carbonated. No α -naphthoic acid was obtained. A second 25-cc. aliquot, withdrawn after eighty minutes and treated as above, also gave no α -naphthoic acid. The remaining 100 cc. of solution was carbonated by the usual procedure and the yield of valeric acid (by titration) was 76.7%. This result is in good agreement with the 75% yield of valeric acid obtained by the carbonation of *n*-butylmagnesium bromide.¹⁰ Apparently, *n*-butyllithium is converted immediately and quantitatively to the corresponding Grignard reagent upon the addition of an excess of magnesium iodide. The reaction can also be reversed, $\text{RMgX} + \text{LiX} \rightleftharpoons \text{RLi} + \text{MgX}_2$, for some unpublished studies by R. N. Meals indicate that some butyllithium

is formed from an excess of lithium bromide with *n*-butylmagnesium bromide.

A mixture of 0.04 mole of methylmagnesium iodide in 50 cc. of ether and 0.025 mole of *n*-butyllithium in 30 cc. of ether showed no halogen-metal interconversion with α -bromonaphthalene. Carbonation yielded 55 mg. of an as yet unidentified bromo acid melting between 260–270°, but no α -naphthoic acid.

No halogen-metal interconversion was noted with α -bromonaphthalene with a mixture of 0.08 mole of ethylmagnesium iodide in 50 cc. of ether and 0.05 mole of *n*-butyllithium in 50 cc. of ether.

Acknowledgment.—The authors are grateful to H. B. Willis for assistance.

Summary

Color tests have been proposed for some organolithium compounds. One of these is useful for differentiating organolithium compounds from the corresponding Grignard reagents, to which they are promptly converted by magnesium iodide. The other is useful, with some limitations, for differentiating alkylolithium compounds from aryllithium compounds.

(10) Gilman and Parker, *THIS JOURNAL*, **46**, 2816 (1924).

AMES, IOWA

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Acetylenic Ethers. I. Phenoxyacetylenes

BY THOMAS L. JACOBS, RICHARD CRAMER AND F. T. WEISS

Although acetylenic compounds in which the triple-bond carbon is directly attached to oxygen have been mentioned in several places¹ and have been postulated as intermediates in organic reactions as recently as 1937,² phenoxyacetylene and benzoylphenoxyacetylene are the only compounds of this type which have been isolated.³ Phenoxyacetylene was an unstable oil which became a black, viscous mass in a few hours. Its structure was confirmed by analysis and by analyses of the explosive silver and copper derivatives. The substance thought to be benzoylphenoxyacetylene was a stable solid.

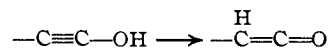
Acetylenic ethers are of interest because they are

(1) (a) Sabanejeff and Dworkowitsch, *Ann.*, **216**, 279 (1883); (b) Nef, *ibid.*, **298**, 337 (1897); (c) Lawrie, *Am. Chem. J.*, **36**, 487 (1906); (d) Grignard and Perrichon, *Ann. chim.*, [10] **5**, 5 (1926); (e) Reihlen, Friedolsheim and Oswald, *Ann.*, **465**, 84 (1928).

(2) Rhinesmith, The action of the Grignard reagent on esters of propiolic acid. A paper presented before the Organic Section of the American Chemical Society at the Rochester meeting, 1937.

(3) Slimmer, *Ber.*, **36**, 289 (1903). The work was done in Nef's laboratory at the University of Chicago.

derivatives of an "yne-ol" system related to aldo-ketenes.



Since such ketene derivatives as ketene acetals⁴ are unusually reactive and enol ethers possess an active double bond and are easily hydrolyzed we might expect acetylenic ethers to show considerable reactivity. They might also exhibit some of the peculiarities of halogenated acetylenes.

As a starting point in the study of acetylenic ethers phenoxyacetylene has been obtained by Slimmer's method, its metallic derivatives have been examined and by their use several substituted phenoxyacetylenes in which the acetylenic hydrogen was replaced by alkyl or other groups have been prepared. The parent compound solidifies in dry-ice and can be stored without decomposition at low temperatures. The room tempera-

(4) Beyerstedt and McElvain, *THIS JOURNAL*, **58**, 529 (1936); **59**, 2266 (1937).