

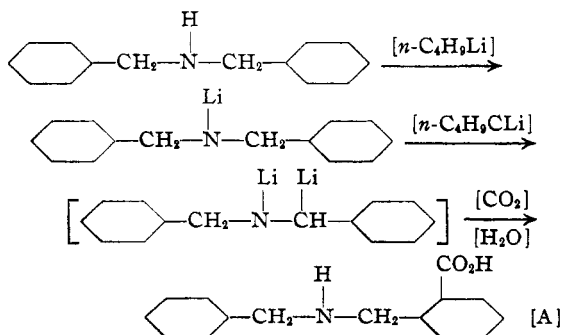
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A Color Test for Some Highly Reactive Organometallic Compounds¹

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Incidental to a study on the introduction of water-solubilizing groups in organometallic compounds, it was observed that some amines like benzylamine give a characteristic color with some highly reactive RM types. This test supplements Color Tests I,^{2a} II,^{2b} and III.^{2c} Like test II, the present test [IV] can be used to differentiate RLi from RMgX compounds, but in a more effective manner for two reasons. First, it is more comprehensive inasmuch as it gives prompt colors with phenyllithium and methyllithium, the latter RLi compound giving no test II. Second, it is more sensitive than II, and only slightly less sensitive than the widely applicable test I which uses Michler ketone.

An examination of the broad applications and limitations of the test has not been completed. However, we are reporting present findings because we have just read an account in *Chemical Abstracts* of closely related work by Krabbe and co-workers.³ Fortunately, their results and ours are complementary, even though there is no complete agreement on some comparable experiments. We have, however, succeeded in throwing a little light on a possible mechanism of the test. When the red solution obtained by reaction of dibenzylamine with *n*-butyllithium is carbonated, there is formed *N*-benzyl- α -amino-*o*-toluic acid [A]. Although this indicates a nuclear metalation, it is probable that a lateral replacement took place first, perhaps of the hydrogen on the nitrogen or hydrogen on the lateral carbon, or both.



(1) Paper XLV in the series "Relative Reactivities of Organometallic Compounds"; the preceding paper is in *THIS JOURNAL*, **64**, 1007 (1942).

(2) (a) *THIS JOURNAL*, **47**, 2002 (1925); (b) *ibid.*, **62**, 1847 (1940); (c) *ibid.*, **63**, 839 (1941).

(3) Krabbe, Grünwald, Polzin, and Menzel, *Ber.*, **74**, 1343 (1941) [*C. A.*, **36**, 5150 (1942)]; see also Stoelzel, *Ber.*, **74**, 982 (1941).

A lateral metalation of an α -carbon atom is to be expected as one stage of the process in view of the pronounced tendency to such metalation. Furthermore, benzyl-metallic types like benzyllithium and benzylnaodium are colored. The subsequent allylic rearrangement to yield a nuclear substituted product is one which finds adequate support from numerous earlier observations.⁴ On such a basis it is understandable why benzylamine and dibenzylamine give color tests. However, it is not clear why *N,N*-dimethylbenzylamine gives no test, while γ -phenylpropylamine gives a stronger test than β -phenylethylamine. The positive tests with allylamine and diallylamine indicate that the tests may involve resonance forms of colored ions like those of the aromatic series.

Experimental

The color test is carried out by adding 1 cc. of the organometallic solution, without shaking, to 0.5 cc. of an approximately molar solution of benzylamine (or dibenzylamine) in unsaturate-free, dry petroleum ether (b. p. 60–68° was used generally). The appearance of a cherry red color in a few seconds is a positive test. If the RM solution is quite dilute, the color may fade in a few minutes. The shade of the red color depends to some extent on the concentration of the RM solution. The benzylamine should be kept in a stoppered bottle.

Sensitivity Tests.—The *n*-butyllithium used for the sensitivity tests was prepared in ether in the customary manner; filtered under nitrogen to a clear solution; titrated by the benzyl chloride procedure; and then diluted with ether to appropriate concentrations.

I. (a) One cc. of a 0.020 molar solution of the RLi reagent and 0.5 cc. of 1.0 molar benzylamine gave a negative test. (b) Two cc. of a 0.020 molar solution of the RLi reagent and 0.5 cc. of 1.0 molar benzylamine gave a positive test. (c) One cc. of a 0.020 molar solution of the RLi reagent and 1 cc. of a 0.038 molar solution of Michler ketone (test I) gave a positive test. (d) Four cc. of the 0.020 molar solution of the RLi reagent was used in color test II and the test was negative.

These tests as given above were checked twice.

II. (a) One cc. of a 0.030 molar solution of the RLi reagent and 0.5 cc. of the 1.0 molar benzylamine gave a positive test. (b) One cc. of a 0.030 molar solution of the RLi reagent was used in Color Test II and the test was negative. (c) Two cc. of a 0.030 molar solution of the RLi reagent was used in Color Test II and the test was weakly positive.

(4) For a general account of such allylic rearrangements, as well as Color Tests I, II, and III, see Chap. 5 in Gilman, "Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1943.

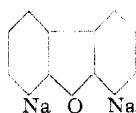
The above tests were checked.

III. The following results were obtained with another preparation of *n*-butyllithium: (a) Two cc. of a 0.023 molar solution of the RLi reagent and 0.5 cc. of 1.0 molar benzylamine gave a positive test. (b) Two cc. of a 0.023 molar solution of the RLi reagent and 0.5 cc. of 1.0 molar dibenzylamine gave a positive test. (c) One cc. of a 0.023 molar solution of the RLi reagent and 0.5 cc. of 1.0 molar dibenzylamine gave a negative test.

Metallic Substances and Amines Examined.—The general results are given in Table I. Absence of color test does not mean that no reaction occurred. For example, the organocalcium compounds reacted, and probably first replaced the hydrogen attached to nitrogen.

TABLE I

METALLIC SUBSTANCES EXAMINED IN COLOR TEST IV	
Positive	Negative
Li, Na, K (freshly cut surfaces)	Ca, Sr, Ba (filings)
CH ₃ Li, C ₂ H ₅ Li, <i>n</i> -C ₄ H ₉ Li, <i>n</i> -C ₆ H ₁₃ Li, C ₆ H ₁₁ Li, C ₆ H ₅ Li, <i>p</i> -ClC ₆ H ₄ Li, <i>p</i> -(CH ₃) ₂ NC ₆ H ₄ Li, 2,3,6-(CH ₃ O) ₃ C ₆ H ₃ Li	CH ₃ MgCl, CH ₃ MgBr, C ₂ H ₅ MgBr, C ₆ H ₅ CH ₂ MgCl, C ₆ H ₅ MgBr, (C ₂ H ₅) ₂ Ca, <i>n</i> -C ₄ H ₉ CaI, C ₆ H ₅ CaI
(CH ₃) ₂ NLi	(C ₂ H ₅) ₂ Zn
<i>n</i> -C ₅ H ₁₁ Na, <i>n</i> -C ₁₅ H ₃₇ Na, C ₆ H ₅ -CH ₂ Na, C ₆ H ₅ Na, C ₂ H ₅ K	



(C₂H₅)₂Sr, (C₂H₅)₂Ba
(C₆H₅)₂Ba

AMINES EXAMINED IN COLOR TEST IV^a

Positive	Negative
C ₆ H ₅ CH ₂ NH ₂	(C ₆ H ₅ CH ₂) ₃ N ^h
(C ₆ H ₅ CH ₂) ₂ NH	C ₆ H ₅ CH ₂ N(CH ₃) ₂
<i>dl</i> -C ₆ H ₅ CH(CH ₃)NH ₂ ^b	CH ₃ NH ₂
C ₆ H ₅ CH ₂ CH ₂ NH ₂ ^b	<i>n</i> -C ₄ H ₉ NH ₂
C ₆ H ₅ CH ₂ CH ₂ CH ₂ NH ₂ ^c	(CH ₃) ₂ NH
CH ₂ =CHCH ₂ NH ₂ ^d	(C ₂ H ₅) ₂ NH
(CH ₂ =CHCH ₂) ₂ NH ^e	HOCH ₂ CH ₂ NH ₂
C ₆ H ₅ NH ₂ ^f	C ₆ H ₅ NH(CH ₃)
β-C ₁₀ H ₇ NH ₂	<i>p</i> -NH ₂ C ₆ H ₄ NH ₂
<i>p</i> -BrC ₆ H ₄ NH ₂ ^g	

^a Approximately one molar solutions in petroleum ether, or benzene if the amine was not soluble in petroleum ether, were used with the various amines. One cc. of one molar methyl lithium in ether was used. ^b A pale orange color developed after one-half hour. ^c The yellow solution changed to red after ten minutes. ^d The orange suspension turned to a red solution after ten minutes. ^e The orange suspension turned only slightly red after ten minutes. ^f A deep brown color developed after four minutes. ^g A reddish brown solution formed in two minutes. ^h No color was observed with *n*-butyllithium after standing five hours.

Metalation of Dibenzylamine.—0.1 mole of *n*-butyllithium in 105 cc. of ether was added over a period of ten minutes to a solution of 9.86 g. (0.05 mole) of dibenzylamine in 25 cc. of ether. The resulting red solution was re-

fluxed for five hours and then carbonated. The residue remaining after the evaporation of the carbon dioxide was treated with 25 cc. of 20% hydrochloric acid and 100 cc. of ether. The mixture was shaken well until the lumps were pulverized and no more reaction was visible. The suspended matter had turned green. The ether was removed and the solid greenish material was filtered off and treated with 55 cc. of 10% potassium hydroxide and 100 cc. of ether and shaken well. The potassium hydroxide solution was removed, warmed to remove any ether, and filtered. This solution was acidified with 10% hydrochloric acid; the excess acid was neutralized with ammonia; and the excess ammonia boiled off. The white precipitate was filtered, and weighed 3.25 g. (27% yield). This acid was dissolved in 25 cc. of 10% potassium hydroxide and just acidified to litmus with 20% hydrochloric acid. Then a few drops of concentrated ammonium hydroxide were added and the solution warmed slightly on a hot-plate to remove the excess ammonia. The acid was filtered off and the above process repeated. The melting point was 164.5–165.5°.⁵

The neutral equivalent was found to be 244.3. The molecular weight of a monocarboxylic compound is 241.28.

Anal. Calcd. for C₁₆H₁₈NO₂: N, 5.81. Found: N, 5.83.

To 1 g. of the above acid was added a solution of 10 g. of potassium permanganate and 20 g. of potassium hydroxide in 200 cc. of water. The resulting mixture was allowed to stand for three hours. Ethyl alcohol was added to destroy all excess potassium permanganate and the mixture filtered and acidified. After working up the oxidation mixture by customary procedure, the white needles obtained melted at 130–131°. A mixed melting point with authentic phthalic anhydride was 130–131°.

Formation of the Lactam of *N*-Benzyl- α -amino-*o*-toluic Acid.—Two-tenths gram (0.0083 mole) of *N*-benzyl- α -amino-*o*-toluic acid was melted in a small beaker. A small amount of methyl alcohol was added to form a homogeneous solution. The solvent was evaporated off and the residue heated to about 140°. This was dissolved in 10 cc. of methyl alcohol, filtered, and heated. To this hot solution was added water, to form a saturated solution. After seeding and cooling, the white needles were filtered off and dried. The yield of lactam was 0.18 g. (97.3%) melting at 89–90°.

Anal. Calcd. for C₁₆H₁₃NO: N, 6.27. Found: N, 6.34, 6.21.

Summary

Some highly reactive organometallic compounds give characteristic colors with amines like benzylamine and dibenzylamine. Lateral metalation, followed by an allylic rearrangement, are apparent stages in the reaction with dibenzylamine.

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(5) Due to the ease with which this acid loses water to form the lactam, the best and most duplicable results on melting point observations were obtained by heating the bath at a rate of about 1° per five seconds and placing the melting point sample in the bath at about 150–155°.