low melting form of α,β-dimorpholinobenzylacetophenone,[2] m. p. 145–152°.

*Anal.* Calcd. for $C_{24}H_{30}N_2O_2$: C, 76.16; H, 7.98; N, 7.40. Calcd. for $C_{25}H_{32}N_2O$: C, 79.77; H, 8.55; N, 7.44. Calcd. for $C_{23}H_{28}N_2O_3$: C, 72.61; H, 7.41; N, 7.36. Found: C, 77.64; H, 8.39; N, 7.41.

It was recrystallized again from the same solvents.

*Anal.* Found: C, 77.61; H, 8.20; N, 7.42.

These experiments were repeated three times and the above described products were obtained each time.

Hydrolysis of the diamino ketone product in the usual way gave a mixture of ω-morpholino- and ω-piperidinoacetophenones, which was isolated as the hydrochloride mixture. This mixture melted at 216–220°.

*Anal.* Calcd. for $C_{12}H_{16}NO_2Cl$: C, 59.64; H, 6.66; N, 5.79. Calcd. for $C_{13}H_{18}NOCl$: C, 65.2; H, 7.57; N, 5.84. Found: C, 63.18; H, 7.21; N, 5.54.

Several recrystallizations from absolute alcohol and dry ether did not change the melting point or composition of this mixture appreciably.

## Summary

1. Further evidence is presented for a proposed mechanism[2] of the reaction of α-bromo-α,β-unsaturated ketones with secondary amines.

2. It has been shown that these reactions may take an abnormal course depending on the characteristics of the secondary amine used.

3. A new α,β-diaminobenzylacetophenone has been prepared.

LINCOLN, NEBRASKA RECEIVED DECEMBER 30, 1940

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# Color Tests for Some Organobismuth and Other Organometallic Compounds[1]

BY HENRY GILMAN AND H. L. YABLUNKY

Different color tests have been proposed for organometallic compounds. The first of these, which is now being designated as Color Test I, is most comprehensive, and has been applied to a wide variety of organometallic compounds. This test uses Michler ketone and is applicable, in general, to all organometallic compounds which add to the carbonyl group in ketones.[2] The second color test[3] (Color Test II) has a two-fold utility. First, it can be used to differentiate organolithium compounds from the corresponding Grignard reagents. Second, it is useful, with some limitations, for differentiating alkyllithium compounds from aryllithium compounds.

The test about to be described, III, appears to be characteristic not only for triarylbismuth dihalides but also for the more reactive *aryl*metallic compounds. Test III is based on the observation of some years ago by Challenger[4a] that a transitory purple color developed when triphenylbismuth dibromide reacted with phenylmagnesium bromide incidental to an attempted preparation of tetraphenylbismuthonium bromide. The reaction apparently did not proceed as expected

$$(C_6H_5)_3BiBr_2 + C_6H_5MgBr \longrightarrow (C_6H_5)_4BiBr + MgBr_2$$

since the only products obtained were triphenylbismuth, diphenylbismuth bromide, phenylbismuth dibromide and bromobenzene. Later, Challenger and co-workers[4b] reported the same intense purple color in attempting to prepare other arylbismuthonium chlorides and fluorides by this reaction. It is unlikely that this reaction can be used to prepare bismuthonium compounds inasmuch as triphenylarsenic dichloride and methylmagnesium iodide gave triphenylarsenic[4c] and not the known stable methyltriphenylarsonium chloride.[4d]

Two suggestions were offered[4b] to account for the transient purple color. One of these was the possible formation of tetraarylbismuthonium halides ($R_4BiX$); and the other was the momentary formation of compounds of the type $R_5Bi$, analogous to the bright red triphenylmethyltetramethylammonium and benzyltetramethylammonium prepared by Schlenk and Holtz.[5] These are the only $R_5$ types reported in Group V. The purple color is probably not due to the formation of a bismuthonium halide because $R_4AsX$[6] and $R_4SbX$

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(1) This is paper XXXV in the series "Relative reactivities of organometallic compounds." Paper XXXIV is in THIS JOURNAL, **62**, 3206 (1940).

(2) Gilman and Schulze, *ibid.*, **47**, 2002 (1925). The most recent study concerned with this color test is by Gilman and Jones, *ibid.*, **62**, 1243 (1940). The latter article has references to several other reports on the range of applicability and degree of sensitivity of the color test.

(3) Gilman and Swiss, *ibid.*, **62**, 1847 (1940).

(4) (a) Challenger, *J. Chem. Soc.*, **105**, 2210 (1914). (b) Challenger and Goddard, *ibid.*, **117**, 762 (1920); Challenger and Wilkinson, *ibid.*, **121**, 91 (1922). (c) Challenger and Allpress, *ibid.*, **119**, 913 (1921). (d) Michaelis, *Ann.*, **321**, 166 (1902).

(5) Schlenk and Holtz, *Ber.*, **49**, 603 (1916); *ibid.*, **50**, 274 (1917).

(6) Blicke and co-workers, THIS JOURNAL, **55**, 3056 (1933); **57**, 720 (1935); **60**, 423 (1938); **61**, 88 (1939).

compounds are colorless. That explanation based on the formation of an $R_5Bi$ compound is somewhat vitiated by the fact that triphenylantimony dichloride, tri-*p*-tolylantimony dichloride, tributylantimony dibromide, or triphenylarsenic dichloride and an arylmagnesium halide do not give a purple color. Although organoantimony and organobismuth compounds have some decidedly different chemical properties, it might be expected that an $R_5Sb$ or $R_5As$ compound, if formed, should also give a purple color. The Experimental Part contains some further observations on possible intermediates.

The color test is carried out readily by adding one cc. of the RM solution to one cc. of an approximately 1% solution of triphenylbismuth dichloride[7] in dry benzene, contained in a small test-tube. With aryllithium and -magnesium compounds a deep purple color forms instantaneously. To detect the presence of other aromatic RM compounds, which do not give this purple color, the test solution, obtained as described above, is heated to boiling, cooled, and hydrolyzed with 1 cc. of water. The benzene layer is then colored yellow, yellow-brown, or yellow-orange when the test is positive. These hydrolysis-colors are obtained also by hydrolyzing the purple colored solutions obtained with RLi and RMgX compounds. No color is obtained before or after hydrolysis when the test is negative.

**Scope of Color Test.**—(1) A large number of triarylbismuth dihalides[8] can be used. This applies to both symmetrical ($R_3BiX_2$) and unsymmetrical ($R_2R'BiX_2$) types. Diarylbismuth halides ($R_2BiX$) and arylbismuth dihalides ($RBiX_2$) do not give the test. Also, no test was observed with some triarylarsenic dihalides and trialkylantimony and triarylantimony dihalides. (2) No alkylmetallic compound like ethylmagnesium bromide, benzyllithium, or phenylethynyllithium gives a color test with a triarylbismuth dihalide. (3) Arylmetallic compounds like Grignard reagents and those more reactive[9] than RMgX compounds give the test.[10] For example, a positive test is obtained with phenylpotassium, but not with tetraphenyllead.

The Experimental Part contains some interesting observations on steric factors.

**Sensitivity.**—The color test is equal in sensitivity to Color Test I which uses Michler ketone,[2] and more sensitive than Color Test II which uses *p*-bromodimethylaniline and triphenylmethane.[3]

**Applications.**—Effective use has already been made of the test in studies on the rates and mechanisms of some metalation and halogen-metal interconversion reactions. For example, alkyllithium compounds (which do not give a positive test) are among reagents of choice in metalations[11]

$$\text{Aryl H} + n\text{-}C_4H_9Li \longrightarrow \text{Aryl Li} + n\text{-}C_4H_{10}$$

and in halogen-metal interconversions,[12]

$$\alpha\text{-}C_{10}H_7Br + n\text{-}C_3H_7Li \longrightarrow \alpha\text{-}C_{10}H_7Li + C_3H_7Br$$

which yield aryllithium compounds at varying rates.

An interesting application of the color test is concerned with the mechanism of metalation of carbazole. Oddo[13] obtained 4-carbazolecarboxylic acid when the reaction mixture of carbazole and methylmagnesium iodide was heated at high temperature in an atmosphere of carbon dioxide. It is known that the —MgI group is initially attached to nitrogen, and that a linkage of this type does not give the color test. However, it is uncertain whether a so-called rearrangement takes place prior to carbonation.

Mr. Clarence G. Stuckwisch has shown that Reaction [A] is more probable because a color test was obtained after heating the —NMgI compound and prior to carbonation.

The color test is not only helpful in reactions involving the more reactive arylmetallic compounds, but may prove of direct value in detecting triarylbismuth compounds (as their dihalides) in disproportionation studies involving related compounds of arsenic and antimony

$$\text{Aryl}_3\text{Sb} + \text{Alkyl}_3\text{Bi} \longrightarrow \text{Aryl}_3\text{Bi} + \text{Alkyl}_3\text{Sb}$$

as well as in some biological studies. For example, Giemsa[14] has examined the applicability of triphenylbismuth in syphilis therapy, and has

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(7) Triphenylbismuth dichloride is technically available, or readily prepared [Michaelis and Marquardt, *Ann.*, **251**, 323 (1889)]. Other triarylbismuth dihalides may be used but are without advantage over triphenylbismuth dichloride.

(8) Preliminary experiments with other salts like triarylbismuth diacetates or dibenzoates have shown that these compounds also give a purple color with aryl Grignard reagents. No tri*alkyl*bismuth dihalide is known.

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

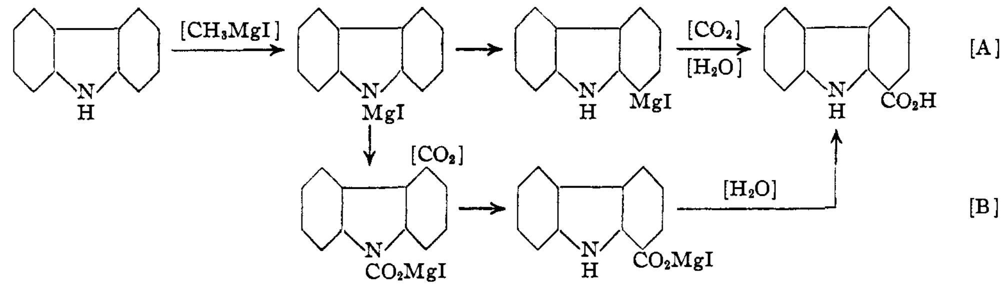
(10) See Experimental Part for a few exceptions.

(11) Gilman and Bebb, THIS JOURNAL, **61**, 109 (1939).

(12) Gilman and Moore, *ibid.*, **62**, 1843 (1940).

(13) Oddo, *Gazz. chim. ital.*, **41**, 255 (1911). See also Gilman and Heck, THIS JOURNAL, **52**, 4949 (1930), on the structures of pyrrylmagnesium halides.

(14) Giemsa, *Dermatol. Wochschr.*, **76**, 523 (1923); **79**, 1567 (1924); *Z. angew. Chem.*, **37**, 765 (1924); *Med. Klin.*, **22**, 60 (1926).



suggested that this organobismuth compound may penetrate the central nervous system without decomposition and then be available for the cure of neurosyphilis. The color test might be applied qualitatively and quantitatively to throw light on the fate of small quantities of triphenylbismuth.

Finally, Color Test III is not only the best procedure for differentiating between reactive alkylmetallic and arylmetallic compounds, but may be preferred by some in studies on arylmagnesium halides and aryllithium compounds because of some conveniences it enjoys over the Michler ketone test.

## Experimental Part

The general procedure for carrying out the color test has been described already. Table I lists the compounds which gave positive or negative tests. The formation of a purple color appears to be specific with the aryllithium and arylmagnesium compounds. This color is stable for about fifteen minutes, and then fades very rapidly. If, however, the purple solution is hydrolyzed, the purple color is rapidly replaced by a deep yellow, yellow-brown or yellow-orange benzene layer. This hydrolysis-color is more generally characteristic of an arylmetallic compound than is the purple color. Every RMgX, $R_2Mg$ and RLi compound which gave a purple color also gave a yellow color on hydrolysis.

Phenylsodium, phenylpotassium, diphenylzinc and tri-*p*-tolylaluminum gave no color on reacting with the $R_3BiX_2$ compound, but hydrolysis gave a deep yellow solution. *n*-Butylsodium gave no color prior to or subsequent to hydrolysis. A "blank" was run simultaneously with every test described in which the RM compound was treated under test conditions but with no $R_3BiX_2$. With but one exception, each blank gave a colorless solution on hydrolysis. To a certain extent the absence of any observable initial color with phenylsodium and phenylpotassium was due to the fact that the samples of these RM suspensions[15] were blackish in color, and this could easily have blotted out any purple color. A similar phenomenon was observed with phenylcalcium iodide, which as ordinarily prepared is intensely dark red. For this reason no color formation was noted on mixing, but hydrolysis gave a yellow colored solution. However, the hydrolysis-color in this particular case is not conclusive, for the blank was slightly yellow in color after hydrolysis.

The negative color test with diphenylberyllium appears to be anomalous, because organoberyllium compounds are generally more reactive than organozinc and organoaluminum compounds.[9] It should be stated that an exothermic reaction occurred on mixing diphenylberyllium with triphenylbismuth dichloride, and the absence of a color may possibly be due to coördination compounds.[16]

**Organobismuth and Other Compounds Used in Color Test III.**—Positive tests were obtained with the following $R_3BiX_2$ compounds: $(C_6H_5)_3BiF_2$, $(C_6H_5)_3BiCl_2$, $(C_6H_5)_3BiBr_2$, $(o\text{-}CH_3C_6H_4)_3BiCl_2$, $(p\text{-}CH_3C_6H_4)_3BiCl_2$, $(p\text{-}ClC_6H_4)_3BiCl_2$, $(p\text{-}ClC_6H_4)_3BiBr_2$, $(o\text{-}CH_3C_6H_4)_2(\alpha\text{-}C_{10}H_7)BiCl_2$, $(p\text{-}CH_3C_6H_4)_2(p\text{-}ClC_6H_4)BiCl_2$, $(C_6H_5)_2(p\text{-}CH_3C_6H_4)BiCl_2$, $(p\text{-}ClC_6H_4)_2(\alpha\text{-}C_{10}H_7)BiCl_2$.

Negative tests were obtained with the following $R_2BiX$ and $RBiX_2$ compounds: $(C_6H_5)_2BiCl$, $(p\text{-}CH_3C_6H_4)_2BiCl$, $(o\text{-}C_2H_5O_2CC_6H_4)_2BiCl$, $o\text{-}CH_3C_6H_4BiBr_2$, and $\alpha\text{-}C_{10}H_7BiBr_2$.

Negative tests were also obtained with $(n\text{-}C_4H_9)_3SbBr_2$, $(C_6H_5)_3SbCl_2$, $(p\text{-}CH_3C_6H_4)_3SbCl_2$, and $(C_6H_5)_3AsCl_2$.

**Sensitivity Tests.—A. *o*-Tolylmagnesium Bromide and Triphenylbismuth Dichloride.**—A solution of *o*-tolylmagnesium bromide, 1.08 molar, and a solution of triphenylbismuth dichloride, 0.078 molar, in benzene, were used in the following tests.

I. (a) One cc. of a 0.038 molar solution of Michler ketone and one cc. of a 0.054 molar solution of the Grignard reagent gave a strong positive test.

(b) One cc. of a 0.078 molar solution of triphenylbismuth dichloride gave a positive test with one cc. of a 0.054 molar solution of the Grignard reagent.

II. (a) One cc. of a 0.038 molar solution of Michler ketone and one cc. of a 0.043 molar solution of the Grignard reagent gave a positive test.

(b) One cc. of a 0.078 molar solution of triphenylbismuth dichloride and one cc. of a 0.043 molar solution of the Grignard reagent gave a positive test.

III. (a) One cc. of 0.038 molar solution of Michler ketone and one cc. of a 0.027 molar solution of the Grignard reagent gave a weak test.

(b) One cc. of a 0.078 molar solution of triphenylbismuth dichloride and one cc. of a 0.027 molar solution of the Grignard reagent gave a very weak test.

IV. (a) One cc. of Michler ketone solution gave a negative test with one cc. of a 0.0213 molar solution of the Grignard reagent.

(b) One cc. of the triphenylbismuth dichloride solution

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[15] Mr. H. A. Pacevitz has prepared phenylsodium as a clear white solid, using a procedure of centrifugal-washing. See, particularly, Schlenk and Holtz, *Ber.*, **50**, 262 (1917).

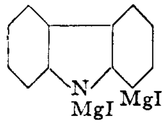
[16] (a) Gilman and Jones, THIS JOURNAL, **62**, 1243 (1940); (b) **62**, 2953 (1940).

TABLE I

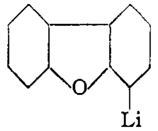
RM COMPOUNDS EXAMINED IN COLOR TEST III

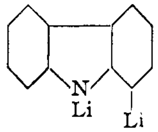
*Positive*

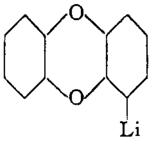
$(C_6H_5)_2Mg$, $C_6H_5MgBr$, *o*-$CH_3C_6H_4MgBr$, $\alpha$-$C_{10}H_7MgBr$, *p*-$CH_3C_6H_4MgBr$, *p*-$ClC_6H_4MgBr$


[a]

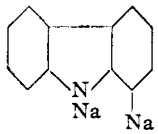
$C_6H_5Li$, *m*-$ClC_6H_4Li$, *p*-$(CH_3)_2NC_6H_4Li$, *p*-$LiO_2CC_6H_4Li$,[b] *p*-$(C_2H_5)_2NSO_2C_6H_4Li$,[c] *o*-$LiC_6H_4SC_4H_9$-*n*[d]






[e]

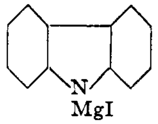
1,2-benzanthryllithium,[f] $C_6H_5Na$

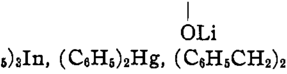


$C_6H_5K$, $(C_6H_5)_2Zn$,[g] (*p*-$CH_3C_6H_4)_3Al$,[g] $C_6H_5CaI$[h]

*Negative*

$C_2H_5MgBr$, *n*-$C_3H_7MgBr$, *n*-$C_4H_9MgBr$, 2,4,6-$(CH_3)_3C_6H_2MgBr$


[i]

$CH_3Li$, $C_2H_5Li$, *n*-$C_4H_9Li$, *t*-$C_4H_9Li$, $C_6H_5CH_2Li$, $C_6H_5C \equiv CLi$,  $2,4,6\text{-}(CH_3)_3C_6H_2\underset{\displaystyle OLi}{\underset{|}{C}}{=}CH_2$[j], *n*-$C_4H_9Na$, $(C_2H_5)_3In$,[k] $(C_6H_5)_3In$, $(C_6H_5)_2Hg$, $(C_6H_5CH_2)_2Hg$, $(C_6H_5)_2(\alpha\text{-}C_{10}H_7)Bi$, [*p*-$(CH_3)_2NC_6H_4]_3Bi$, (*p*-$CH_3C_6H_4)_3Pb$,[l] $(C_6H_5)_4Pb$, $(C_6H_5)_4Sn$

[a] Formed by heating carbazole and methylmagnesium iodide at 260°. Carbonation of the product yielded 4-carbazolecarboxylic acid. [b] Test obtained at −60°, three minutes after mixing *p*-iodobenzoic acid and *n*-butyllithium. [c] Test obtained at −60°; three minutes after mixing *p*-iodo-N,N-diethylbenzenesulfonamide and *n*-butyllithium. [d] Prepared in two ways: from phenyl *n*-butyl sulfide and (1) *n*-butyllithium, and (2) lithium metal. A color test was also obtained from phenyl methyl selenide and *n*-butyllithium, and this was due to phenyllithium formed by cleavage. [e] From diphenylene dioxide and *n*-butyllithium. [f] From 1,2-benzanthrene and *n*-butyllithium. The position of the lithium has not as yet been established. [g] The color tests with diphenylzinc and tri-*p*-tolylaluminum were weak, and developed only on hydrolysis. [h] The color test with phenylcalcium iodide, as mentioned previously, is doubtful. [i] From carbazole and methylmagnesium iodide at room temperature. [j] From acetomesitylene and methyllithium. [k] Prepared by Mr. R. G. Jones from indium and diethylmercury. The authors are grateful to Mr. Jones and other graduate students for several of the RM compounds. [l] Triaryllead compounds have been shown recently to be more reactive than the corresponding tetraaryllead compounds in metal-metal interconversions [Gilman and Moore, THIS JOURNAL, **62**, 3206 (1940)].

(0.078 molar) gave a negative test with one cc. of the 0.0213 molar solution of the Grignard reagent.

V. 0.05 cc. of a 1.08 molar solution of *o*-tolylmagnesium bromide gave a positive test with one cc. of a 0.0078 molar solution of triphenylbismuth dichloride.

Experiments III and IV were checked starting each time with the 1.08 molar Grignard solution and diluting to the desired concentration with identical results.

**B. Phenylmagnesium Bromide and Triphenylbismuth Dichloride.**—One cc. of a 1.15 molar solution of phenylmagnesium bromide was diluted with 49 cc. of ether to give a 0.023 molar solution.

I. (a) One cc. of this 0.023 molar solution gave a positive test with one cc. of a 0.038 molar solution of Michler ketone.

(b) One cc. of this 0.023 molar solution gave a weak purple color with one cc. of a 0.078 molar solution of triphenylbismuth dichloride.

This was the maximum dilution in either case which gave a positive color test. Test I was checked four times, starting each time with one cc. of the 1.15 molar solution and diluting to fifty cc. with ether. These tests confirm the data obtained with *o*-tolylmagnesium bromide, where the maximum dilution was 0.027 molar.

II. One cc. of a 1.15 molar solution of phenylmagnesium bromide gave a weak positive test with one cc. of a 0.0039 molar solution of triphenylbismuth dichloride. Three cc. of this same Grignard solution gave a negative test with one cc. of an 0.003 molar solution of triphenylbismuth dichloride. From this it appears that a limiting factor in the sensitivity of Color Test III is the concentration of the $R_3BiX_2$ compound.

It will be noted that the sensitivity of the Michler ketone test for phenylmagnesium bromide is greater than that reported.[16a] This is due, in part, to the following modified technique. A flask was flushed thoroughly with nitrogen; the ether (49 cc.) was added; and then nitrogen was bubbled through the ether for about one minute, thereby providing the flask with an atmosphere of ether vapor and nitrogen. Then the tip of the pipet containing one cc. of the standard Grignard solution was placed below the surface of the ether and the contents of the pipet were allowed to drain. The ether solution was whirled vigorously and this dilute solution was ready for use. In the earlier pro-

TABLE II

EFFECT OF SOME STERIC FACTORS ON COLOR TEST

| $R_3BiX_2$ or $R_2R'BiX_2$ compound | RM Compound | Intensity of purple color |
|---|---|---|
| Tri-*p*-chlorophenylbismuth dichloride | $\alpha$-$C_{10}H_7MgBr$ | Strong |
| Di-*p*-chlorophenyl-$\alpha$-naphthylbismuth dichloride | $\alpha$-$C_{10}H_7MgBr$ | Very weak |
| Di-*p*-chlorophenyl-$\alpha$-naphthylbismuth dichloride | *p*-$CH_3C_6H_4MgBr$ | Strong |
| Tri-2-*p*-cymylbismuth dichloride | *p*-$CH_3C_6H_4MgBr$ | Negative |
| Tri-2-*p*-cymylbismuth dichloride | $C_6H_5MgBr$ | Negative |
| Tri-2-*p*-cymylbismuth dichloride | $\alpha$-$C_{10}H_7MgBr$ | Negative |
| Di-*o*-tolyl-$\alpha$-naphthylbismuth dichloride | $C_6H_5MgBr$ | Very weak |
| Di-*o*-tolyl-$\alpha$-naphthylbismuth dichloride | $\alpha$-$C_{10}H_7MgBr$ | Negative |
| Di-*o*-tolyl-$\alpha$-naphthylbismuth dichloride | *p*-$CH_3C_6H_4MgBr$ | Very weak |

cedure[16a] the large volume of ether was added to the small volume of Grignard reagents.

**Some Steric Factors.**—We have found that steric factors either in the RM compound or in the $R_3BiX_2$ compound decrease the intensity of the purple color, or may in some instances prevent its formation. For example, triphenylbismuth dichloride or tri-*p*-tolylbismuth dichloride (or dibromide) and mesitylmagnesium bromide gave no purple color, whereas with *o*-tolylmagnesium bromide a very intense purple color was obtained. Tri-*o*-tolylbismuth dichloride gave a weak purple color with phenylmagnesium bromide and with *p*-tolylmagnesium bromide, but a negative test with $\alpha$-naphthylmagnesium bromide. Trimesitylbismuth dichloride gave a negative test with these three Grignard reagents. It is also of interest to note that Challenger and Allpress[4c] reported no purple color in the reaction between tri-$\alpha$-naphthylbismuth dibromide and phenylmagnesium bromide. Table II summarizes other related reactions which indicate the role played by steric factors in this color test.

**Miscellany.**—The following orienting experiments were carried out in connection with possible mechanisms of reaction.

To a solution of *o*-tolylmagnesium bromide (taken in excess) was added 4 g. of triphenylbismuth dichloride in small portions and with stirring. The solution assumed a purple color; considerable heat was evolved; and the color disappeared after one hour. After standing overnight, the mixture was poured upon ice; the aqueous suspension extracted with ether; and the ether extract removed. From the ether solution was obtained (by alkali extraction) *o*-cresol, identified as the aryloxyacetic acid (mixed melting point).[17] Because the yield of *o*-cresol was only 0.1 g. it appears more reasonable to attribute its formation to incidental oxidation of the Grignard reagent rather than to the formation of an $R_4BiOH$ compound which might have decomposed into $R_3Bi$ and ROH. This does not, of course, rule out the possibility that the hydrolysis-color may be due to a quinoidal structure.

Triphenylbismuth and phenylmagnesium bromide give no color, indicating in all probability that an $R_4BiMgBr$ compound, if formed, is not the source of the color. Experiments are in progress on the isolation of possible radicals and other intermediates in the color test.

**Michler Ketone Test (I) with $R_2Mg$ Compounds.** (By R. G. Jones.)—A question has been raised whether $R_2Mg$ compounds will give a Michler ketone test like RMgX compounds or whether coördination compounds[16a] would interfere with the test. We have observed that diphenylmagnesium, prepared from diphenylmercury and magnesium[18] (and free of halogen), does give a positive test. Furthermore, diphenylmagnesium forms a coördination compound with Michler ketone, and hydrolysis of the complex regenerates part of the ketone. Actually, the reactions between Michler ketone and either diphenylmagnesium or phenylmagnesium bromide in ether–benzene solution give almost identical results. One equivalent of phenylmagnesium bromide with Michler ketone gave 45% of unchanged ketone and 42% of *p,p'*-tetramethyldiaminotriphenylcarbinol[16a]; whereas the yields of ketone and carbinol when diphenylmagnesium was used were 45 and 39.5%, respectively. Even when two equivalents of diphenylmagnesium were allowed to react with Michler ketone, a small quantity (2.3%) of the latter was recovered unchanged subsequent to hydrolysis.

One noteworthy difference was observed in the color test with diphenylmagnesium. Whereas phenylmagnesium bromide gives an orange precipitate with Michler ketone, diphenylmagnesium with Michler ketone gives a clear, colored solution.

It is highly probable that di*alkyl*magnesium compounds will, in general, give the Michler ketone test, for Brown has shown that di-*n*-butylmagnesium[19a] and dimethylmagnesium[19b] give the color test.

To a suspension of 1.34 g. (0.005 mole) of Michler ketone in a mixture of 20 cc. of dry ether and 20 cc. of dry benzene (in a dry nitrogen atmosphere) was added 5 cc. of a 0.56 molar ether–benzene solution of diphenylmagnesium. The ketone dissolved immediately to give a clear, brownish-orange solution. After stirring for fifteen minutes at room temperature, the solution was hydrolyzed with 50 cc. of a 5% ammonium chloride solution and then worked up in a previously described manner.[16a] The ketone (45% yield) and the carbinol (39.5% yield) were identified by the method of mixed melting points. In a check experiment the yield of carbinol was 40%, and the yield of ketone, 45.5%. When an experiment was carried out with 10 cc. of the diphenylmagnesium solution (0.112 equivalent) and 1.34 g. (0.005 mole) of Michler ketone, the yield of carbinol was 79.5% and the yield of ketone was 2.3%.

**Metalation of Carbazole.** (By C. G. Stuckwisch.)—The mechanism [A] suggested in the introductory material for

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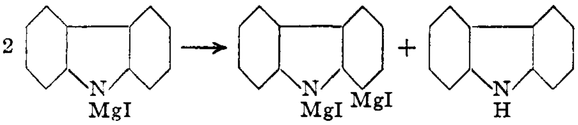
[17] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1935, p. 90.

[18] Gilman and Brown, *Rec. trav. chim.*, **49**, 202 (1930).

[19] (a) Gilman and Brown, *ibid.*, **49**, 724 (1930); (b) **48**, 1133 (1929).

the presence of a —CMgI linkage in carbazole, after heating but before carbonation, may not be complete. It is quite possible that one molecule of the precursory —NMgI compound may have metalated another like molecule to give a di-MgI compound and carbazole. The di-MgI compound would give a positive color test III because of the presence of a true arylmagnesium iodide unit. Carbonation of such a compound might be expected to give a carbamic-carboxylic acid which would readily lose carbon dioxide to yield the 4-carbazolecarboxylic acid which was isolated.



[C]

To a solution of methylmagnesium iodide prepared from 11 g. (0.075 mole) of methyl iodide and 2.5 g. (0.1 g. atom) of magnesium in 100 cc. of ether was added 8.5 g. (0.042 mole) of carbazole. The solution was stirred and refluxed for one hour. At this time Color Test III was negative and Color Test I was positive. The ether was evaporated and the residual solid was heated to 260° for ten minutes and allowed to cool. Color Test III at this point was strongly positive. The mixture was again heated to 260° and carbonated with gaseous carbon dioxide for three hours. Sublimed carbazole was evident on the cool upper parts of the flask previous to carbonation. On working up the reaction mixture there was obtained 27% of 4-carbazolecarboxylic acid (mixed m. p.), and the recovery of carbazole was 70%.

In an identical experiment, the reaction mixture after removal of the ether and heating at 260° for ten minutes was cooled, the solid mass was disintegrated and warmed with 50 cc. of ether for one-half hour. Solution occurred with difficulty and was by no means complete. The suspension was poured on powdered dry-ice. The yield of 4-carbazolecarboxylic acid was 5%. The low yield was due probably to the difficulty encountered in dissolving the reaction solid.

To eliminate the possibility that the metalation of carbazole may have occurred with the excess methylmagnesium iodide present in the two above-described experiments, a third experiment was carried out between 0.052 mole of carbazole and methylmagnesium iodide (from 0.035 mole of methyl iodide and 0.05 g. atom of magnesium). Color Tests I and III were both negative before heating, but after heating to 260° both tests were positive. Subsequent to carbonation at 260° there was obtained a 15% yield of 4-carbazolecarboxylic acid.

A final experiment was carried out with a view of shedding some light on the ability of an =NMgX compound to metalate an RH compound, as postulated in Reaction [C]. To a solution of methylmagnesium iodide (prepared from 0.075 mole of methyl iodide) was added 0.08 mole of di-*n*-butylamine. At this point both color tests were negative. Four-hundredths mole of N-ethylcarbazole was added, the ether evaporated, and the residual solid heated to 260°. Both color tests were still negative. Carbonation was carried out at this temperature in the usual manner. No acidic material was obtained.

The Zerewitinoff technique used by Gilman and Heck[13] for determining the structure of the pyrrylmagnesium halides is probably not applicable to carbazole because of the drastic temperature (260°) used by Oddo. Active hydrogen measurements at such a temperature might be difficult and without much validity because of the lack of a suitable medium and because of the highly probable extensive thermal decomposition of Grignard reagents at that temperature.

**Interference Effects of Some Compounds.**—It has long been known that some acid halides and some inorganic halides interfere with the Michler ketone color test.[20] Apparently, some of these compounds also interfere with the Color Test III.

The color test between triphenylbismuth dichloride and phenylmagnesium bromide is affected by inorganic halides like aluminum chloride, mercuric chloride, bismuth chloride and cuprous chloride. The characteristic purple color forms, but instead of persisting as usual for about fifteen minutes, it dissipates rapidly even in the presence of traces of these salts and is gone entirely in about one minute. In some instances, this colorless or yellow solution gives a yellow solution on hydrolysis, but this ordinarily confirmatory hydrolysis-color is no longer reliable.

Some acid halides like benzoyl chloride also interfere in the color test, and the phenomena are very similar to those described with the inorganic halides.

## Summary

Triarylbismuth dihalides give characteristic colors with reactive arylmetallic compounds. This color test (III) is equal in sensitivity to the Michler ketone test (I), and is more sensitive than the organolithium tests (II) described recently. The color test III is one of choice for differentiating reactive arylmetallic compounds from corresponding reactive alkylmetallic compounds, and appears to be of definite diagnostic value for detecting triarylbismuth compounds as their dihalides.

Observations have been made on the effects of steric hindrance, the probable structure of carbazolemetallic compounds, and on coördination compounds between diphenylmagnesium and Michler ketone.

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[20] Gilman and Heck, THIS JOURNAL, 52, 4949 (1930).