TWO NEW COLOR TESTS FOR DETERMINING THE PRESENCE OF ARYLMETALLICS*

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INTRODUCTION

Gilman's Color Test III[1] is the usual method for determining the presence of an active arylmetallic reagent, but it requires the use of triphenylbismuth dihalides, materials not commercially available and not indefinitely stable. Color Test I[2,3] probably the most widely used color test in organometallic chemistry, indicates the presence of active organometallics without distinguishing between alkyl- and arylmetallic compounds. This test may be modified in two simple and different ways to enable it to determine the presence of an arylmetallic reagent in a mixture, thus performing the function of Color Test III. The modified tests use readily available chemicals.

The first step in Color Test I is addition of the organometallic reagent to Michler's ketone [4,4'-bis(N,N-dimethylamino)benzophenone]. This is followed by acid hydrolysis** to give a colored cation:

$$(Me_2NC_6H_4)_2C{=}O \xrightarrow{RM} (Me_2NC_6H_4)_2RCOM$$

$$\xrightarrow{H_2O} (Me_2NC_6H_4)_2RCOH + MOH$$

$$\xrightarrow{H^+} (Me_2NC_6H_4)_2RC^+ + H_2O$$

If R is aryl, the last step occurs relatively easily because conjugation lowers the energy of the carbonium ion. Acetic acid, normally used in this test, produces ions whether R is alkyl or aryl, but in principle it is possible to use an acid so weak that ions form only if R is aryl. Catechol (1,2-dihydroxybenzene) is a suitable acid in the first modification of Color Test I, which will be designated Color Test IC, the C denoting catechol.

Ar_2RCOH (Ar = $PhNMe_2$) is ionized in weak acids like catechol only if R is aryl. It is ionized in stronger acids (like 1 N acetic) whether R is alkyl or aryl. In much stronger acids, like 1 N HSO_4^-, it is ionized and then protonated in a dimethylamino group to give the dication $HMe_2N^+{-}C_6H_4{-}^+CR{-}C_6H_4{-}NMe_2$. This dication is stable for R = aryl and is green in color. If however, R = alkyl, the carbonium ion center reacts rapidly with a nucleophile X^- to give the colorless ammonium ion $HMe_2N^+{-}C_6H_4{-}CRX{-}C_6H_4{-}NMe_2$. This is the basis of the second modified color test, which will be designated Color Test IB, the B denoting bisulfate ion.

Gilman's original test will be referred to hereafter as Color Test IA, where the A denotes acetic acid.

EXPERIMENTAL

Color Test IC

To 1 ml of 1% Michler's ketone in benzene was added 0.05 ml of an approximately $2 M$ solution of the organometallic reagent, followed by 0.5 ml of distilled water. To this mixture was added one to two ml of 20% aqueous catechol and then one to five drops of 0.5% I_2 in benzene. If the reagent was aryl, a green to blue color appeared in the upper (organic) layer and remained *even after thorough shaking*. If the reagent was alkyl, no color appeared. One to ten drops of glacial acetic acid was then added, and resulted either in intensification of the color already there for aryl reagents or development of color in the lower (aqueous) layer for alkyl reagents. The sensitivity of Color Test IC is about $\frac{1}{5}$ as great as Color Test IA; that is, 15 drops of 0.2 M PhLi are needed to give the same depth of coloration as 3 drops of 0.2 M PhLi in Color Test IA. Results are shown in Table I.

TABLE 1

RESULTS PERTAINING TO COLOR TEST IC

| Organometallic reagent | Color (upper layer/lower layer) after adding | |
	catechol	acetic acid
1 Phenyllithium/benzene+Et_2O	Green/colorless	More intense
2 Phenylmagnesium bromide/Et_2O	Green/colorless	More intense
3 Mesityllithium/Et_2O	Blue/colorless	More intense
4 2-Tolylmagnesium bromide/Et_2O	Blue green/colorless	Blue green/deep blue
5 2-Ethylphenylmagnesium bromide/Et_2O	Green/colorless	Green/blue
6 2-Biphenylylmagnesium bromide/Et_2O	Blue green/colorless	Green/blue green
7 2-Lithio-2'-lithioxybiphenyl[5]/Et_2O + hexane	Essentially colorless	Colorless/green
8 Methyllithium/Et_2O	Colorless	Colorless/blue
9 Ethylmagnesium bromide/Et_2O	Colorless	Colorless/blue
10 n-Butyllithium/hexane	Colorless	Colorless/blue
11 sec-Butyllithium/hexane	Colorless	Colorless/blue
12 tert-Butyllithium/pentane	Colorless	Colorless/blue
13 Vinyllithium/THF	Colorless, but slowly develops faint green	Colorless/blue
14 Vinylmagnesium chloride/THF	Colorless, but slowly develops faint green	Colorless/blue
15 Phenyllithium + n-Butyllithium/ benzene + Et_2O + hexane	Green/colorless	More intense
16 Triethylaluminum/benzene	Weak green/colorless	Weak green throughout
17 Diethylzinc/benzene	Colorless	Colorless

Other weak acids may be used instead of catechol:

Catechol pK_{a1} 9.4
Resorcinol pK_{a1} 9.4

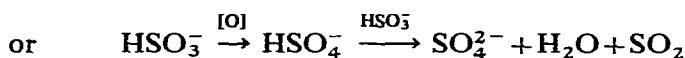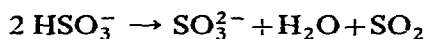|	
Sodium bisulfite	$pK_{a2}H_2SO_3$ 6.91
Ammonium chloride	pK_a 14 − 4.75 = 9.25
Glycine	pK_a 9.87
Sodium bicarbonate	eff. $pK_{a2}(H_2CO_3)$ 10.25
	theor.[6] $pK_{a2}(H_2CO_3)$ 7.52

but not

Boric acid (15% in methanol)	pK_{a1} 9.14
Dimethylammonium chloride	pK_a 14 − 3.28 = 10.72
Potassium dihydrogen phosphate	$pK_{a2}(H_3PO_4)$ 7.21
Aniline hydrochloride	pK_a 14 − 9.42 = 4.58

The acids that did not work were either too strong or too weak. It should be noted that aqueous pK_a's are not completely reliable for predicting acidity in the organic layer, where color appears for aryl reagents. Even the acids that do work are subject to certain disadvantages:

(1) Aqueous solutions of catechol and resorcinol turn dark on storage. Fresh solutions should be made monthly because Color Test IC becomes less delicate if the acid solution is very dark. In some cases it may be more convenient to add the solid acid, which is quite stable.

(2) Sodium bicarbonate is a little too strong, and faint colors often appear with alkyl reagents. It must be added as a solid because of its low solubility in water.

(3) Sodium bisulfite works in fresh solutions (even if contaminated with small amounts of bisulfate), but after about one month's exposure to air, the acid content of the solution decreases to 20% of that calculated for $NaHSO_3$, probably by elimination of SO_2:

$$2\ HSO_3^- \rightarrow SO_3^{2-} + H_2O + SO_2$$

or $\quad HSO_3^- \xrightarrow{[O]} HSO_4^- \xrightarrow{HSO_3^-} SO_4^{2-} + H_2O + SO_2$

(4) Ammonium chloride and glycine are very slow (color develops only after about 10 minutes at room temperature, with or without iodine) but their action may be accelerated by warming the solution in which a color is expected.

Color Test IB

To 1 ml of 1% Michler's ketone in benzene was added 0.05 ml of an approximately 2 M solution of the organometallic reagent, followed by 0.5 ml of distilled water. The mixture was acidified with 5 to 15 drops of glacial acetic acid and shaken well. The color was noted. One to two ml of 20% aqueous $NaHSO_4$ was then added, the mixture was shaken, and the color was noted again. In all cases, aryl reagents gave a green color after treatment with $NaHSO_4$, and alkyl reagents gave a colorless solution. The sensitivity of modification Color Test IB is essentially the same as that of Color Test IA. If desired, Color Test IB may be performed on the solution resulting from Color Test IA, which may in turn be performed on the solution resulting from Color Test IC. Results are shown in Table 2.

TABLE 2

RESULTS PERTAINING TO COLOR TEST IB

Organometallic reagent	Color (upper layer/lower layer) after adding	
	acetic acid	HSO_4^-
1 Phenyllithium/benzene + Et$_2$O	Deep blue green throughout	Light blue/deep green
2 Phenylmagnesium bromide/Et$_2$O	Light blue/deep blue	Light green/deep green
3 Mesityllithium/Et$_2$O	Deep blue throughout	Light blue/deep green
4 2-Tolylmagnesium bromide/Et$_2$O	Light green/deep blue	Light blue/green
5 2-Ethylphenylmagnesium bromide/Et$_2$O	Green/blue	Blue/light green
6 2-Biphenylylmagnesium bromide/Et$_2$O	Green/blue green	Light green/deep green
7 2-Lithio-2'-lithioxybiphenyl[5]/Et$_2$O + hexane	Colorless/green	Colorless/green
8 Methyllithium/Et$_2$O	Colorless/blue	Colorless
9 Ethylmagnesium bromide/Et$_2$O	Colorless/blue	Colorless
10 n-Butyllithium/hexane	Blue/green	Colorless
11 sec-Butyllithium/hexane	Colorless/blue green	Colorless
12 tert-Butyllithium/pentane	Colorless/blue green	Colorless
13 Vinyllithium/THF	Light blue green/deep blue	Colorless/medium green
14 Vinylmagnesium chloride/THF	Light green/deep blue	Colorless/light green
15 Phenyllithium + n-Butyllithium/benzene + Et$_2$O + hexane	Deep blue green throughout	Light blue/deep green

S-butyllithium and tert-butyllithium gave blue green colors if a small amount (0.02 ml) of the organometallic reagents was added to the Michler's ketone solution, but gave a red-brown color if added more liberally (0.10 ml). However, the red-brown solution also turned colorless when treated with sodium bisulfate. This is apparently an example of concentration-dependent dichroism in the ion.

Color Test I.A

Acetic acid is one of many acids that may be used in Gilman's original color test. The following ten acids may be used:

Acetic	pK_a 4.75	but not	
Bromoacetic acid	pK_a 2.69		
Chloroacetic acid	pK_a 2.85	Oxalic acid	pK_{a1} 1.23
Dichloroacetic acid	pK_a 1.48	15% NaHSO$_4$	$pK_{a2}(H_2SO_4)$ 1.92
Formic acid	pK_a 3.75	Trichloroacetic acid	pK_a 0.70
Itaconic acid	pK_{a1} 3.85	Tartaric acid (with I$_2$)	pK_{a1} 3.22
KH$_2$PO$_4$ (with I$_2$)	$pK_{a2}(H_3PO_4)$ 7.21	Citric acid (with I$_2$)	pK_{a1} 3.08
Salicylic acid	pK_a 3.00	Malonic acid (with I$_2$)	pK_{a1} 2.83
DL-Mandelic acid	pK_a 3.85	DL-Malic acid (with I$_2$)	pK_{a1} 3.40
Hydrofluoric acid	pK_a 3.45	Oleic acid (with I$_2$)	pK_{a1} 5.00

The acids that did not work were either too strong (oxalic acid and HSO_4^-), or gave an unexpected color (Cl_3CCO_2H gave green for BuLi instead of blue), or were too slow (even with I$_2$ catalysis), perhaps because of solubility problems. Acetic acid is the acid of choice in this test and its modifications.

DISCUSSION

The variations in color from blue to green often seen in Color Test IA are not characteristic of alkyl or aryl groups in the organometallic reagent. If the intensely colored test solution of Color Test IA is diluted with about 50 volumes of water/benzene/ether mixture, a blue color localizes in the aqueous layer for alkyl and aryl reagents alike, so a distinction cannot be made between them on the basis of color or preference for aqueous or organic layer. The third aryl group in a triaryl carbonium ion has almost no effect on λ_{max}, e.g. Ph_3C^+ (λ_{max} 4340 Å) and Ph_2HC^+ (λ_{max} 4420 Å)[7] absorb at almost the same wavelength, as do (p-MeOC$_6$H$_4$)$_3$C$^+$ (λ_{max} 4850 Å) and (p-MeOC$_6$H$_4$)$_2$HC$^+$ (λ_{max} 5070 Å)[8]. This effect is not limited to triarylmethyl cations; the cations formed from xanthone plus butyllithium or phenyllithium have the same deep yellow color. The reason that λ_{max} does not change much with aryl substitution is that the highest filled molecular orbital and the lowest vacant molecular orbital are both lowered equally[9] (see Fig. 1).
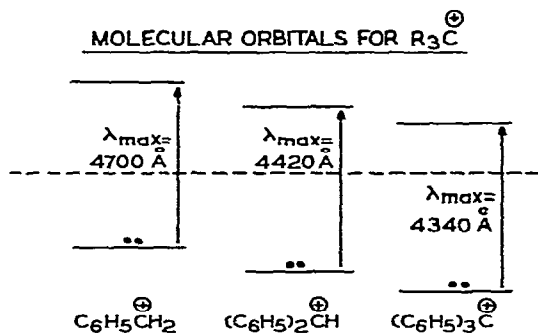
Fig. 1. Molecular orbitals for R_3C^+.

Although the color of the ions is sensibly constant, their readiness to ionize increases appreciably with aryl substitution. The triaryl ion is formed more than 10^6 times easier than the diaryl in each case. This large difference in $pK_{(R+)}$[8] allows an acid to be selected that will produce a significant quantity of triarylmethyl ions without producing a noticeable concentration of diarylalkylmethyl ions. The acid of choice in the first modification, Color Test IC, is catechol because of its availability and stability (at least when solid). All water-soluble phenols with the proper acidity are subject to darkening by oxidation, but no other acids seem to work as well.

Several peculiarities of the modified test are worthy of note. It was necessary to shake the tests for organomagnesium compounds vigorously to insure complete mixing; otherwise the Mg(OH)$_2$ from hydrolysis coagulated and did not prevent the appearance of a color from an alkyl reagent. Even violent shaking did not remove the weak green color developed in the test for triethylaluminum. Metal hydroxide from hydrolysis of the Li or Mg carbinolates reacts with catechol to give an aqueous solution buffered near pH 9 by roughly equal concentrations of catechol and catecholate ions. An alkyl-substituted carbinol, unionized at this pH, gives a colorless solution. Alkylaluminum reagents give rise to the weak base Al(OH)$_3$, which does not react with catechol to give catecholate. The resulting solution is not buffered; it is so acidic that a weak color is generated, falsely indicating aryl. Color Test IC is

not applicable to organometallic reagents dissolved in triethylamine because the amine makes the aqueous solution too basic. Diethylzinc does not add to carbonyl groups, hence gives no color reaction at all.

When the solution of the colored carbonium ion resulting from Color Test IA is made more strongly acid in Color Test IB, protonation of a dimethylamino group occurs[10,11]. The carbonium ion center then acquires enhanced reactivity because of the curtailment of π-donation from this dimethylamino group. The remaining dimethylanilino group in $HNMe_2C_6H_4-{}^+CR-C_6H_4NMe_2$ increases $pK_{(R^+)}$ by 12 over hydrogen, but the positive carbon retains considerable reactivity unless further stabilized by the R group. If R is aryl [e.g. phenyl, which increases $pK_{(R^+)}$ by 6 over hydrogen], the green carbonium ion is stable in aqueous acid. If R is alkyl, however, the positive carbon is attacked by some negative nucleophile X^- or perhaps by H_2O to give the carbinol-ammonium ion. In either event, the product is colorless because it will not dissociate in acid of this strength.

Three organic groups behaved irregularly: (1) The vinylmetallic reagents developed no immediate color in the catechol solution, but did give a faint green after standing 10 to 30 minutes or faster on warming. This effect is unrelated to THF (common solvent to both), for n-BuLi in hexane plus THF reacts just as n-BuLi does in hexane alone. The vinyl reagents did give an immediate color with acetic acid, but the color was concentrated mostly in the upper layer, as with aryl reagents. The vinyl group, which would have π-donor properties intermediate between alkyl and aryl[12], might be expected to give a weak color in Color Test IC, but the delayed color development is puzzling. It may be that poorly stabilized carbonium ions are formed only slowly in weak acid, even with iodine catalysis, or the color may be due to coupling and rearrangement products[7,13]. (2) The color for Ar_2C^+R (R = mesityl) appears with catechol and concentrates in the upper layer. Thus mesityl unexpectedly behaves like an ordinary aryl group in both modified tests even though the 3 rings cannot be even nearly coplanar in the carbonium ion*. We conclude that the primary effect of mesityl in Color Test IC is to introduce steric strain in the molecule which is relieved upon ionization. This hypothesis is supported by the fact that dimesitylmethanol in sulfuric acid ionizes about as readily as triphenylmethanol and much more completely than diphenylmethanol or di-p-tolylmethanol[8]. Furthermore, 4,4'-bis(dimethylaminophenyl)-2",6"-dimethylphenyl carbonium ion (lacking only the p-methyl group of being the same compound observed) does not react with hydroxide ion to give the carbinol, but undergoes decomposition instead[15]. In Color Test IB, protonation of one dimethylamino group would severely reduce the π-donor properties of an Ar group in Ar_2RC^+. This Ar group would then have little or no preference for coplanarity with the sp^2 central carbon. The other two groups on the central carbon might then be freer to approach planarity with the sp^2 carbon, even if one is mesityl. (3) 2-Lithio-2'-lithioxybiphenyl, (I), gave a negative color test in Color Test IC, but reacted normally in Color Test IA and Color Test IB. Michler's ketone plus (I) would give (II) at first, but this would be hydrolyzed to the diol (III). Dehydration then occurs to give (IV)**, which must be covalent rather than zwitterionic, for the

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* It should be noted that the Ph_3C^+ ion is non-planar[14], each ring being twisted out of the plane by about 30°.
** The alternative is to assume that (III) is the end product but does not give the carbonium ion under conditions which are sufficient to produce the carbonium ion from $2-C_6H_5-C_6H_4-C(OH)Ar_2$.

zwitterion (intramolecular ion pair) would be colored[16]. Catechol is too weak an acid to split the cyclic ether (IV), but acetic acid gives the carbonium ion, which is stable even in $NaHSO_4$.
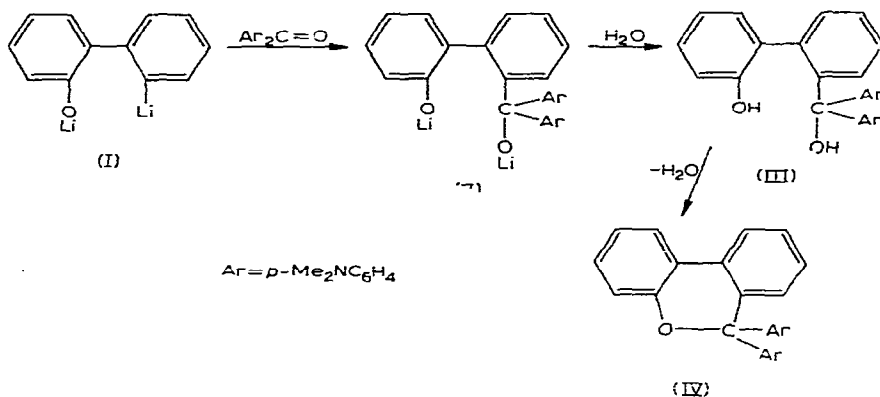
In an attempt to determine the function of the iodine, which has been used since the origination of the test, the following was observed:
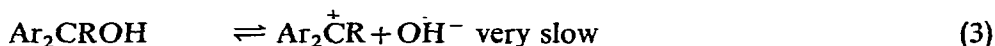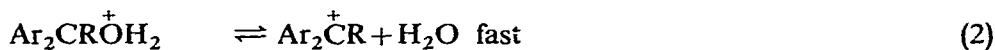
(1) If an active arylmetallic reagent is added to Michler's ketone, hydrolyzed and then acidified with acetic acid, color develops instantly. Iodine *is not needed*. If catechol is substituted for acetic acid, color develops slowly (2 to 10 minutes), unless iodine is added. The addition of iodine causes immediate color development.

(2) If the color is allowed to develop for about 10 minutes with catechol alone, addition of iodine causes no further color development.
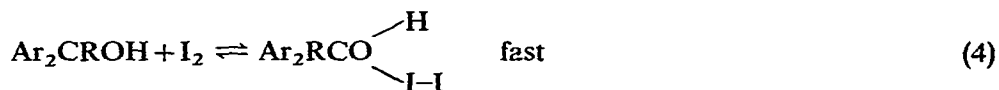
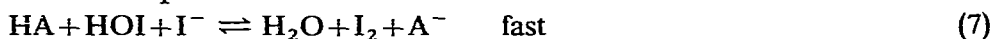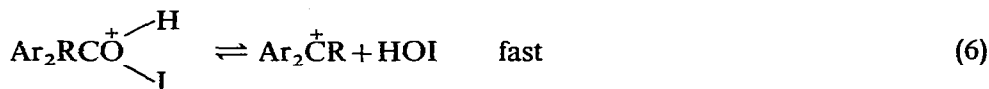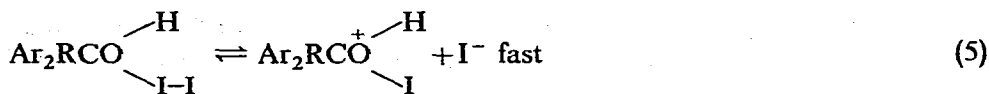(3) Hydrogen peroxide is not an agent for color development.

(4) Iodine does not acelerate the development of color if the acid used is am-amonium chloride or glycine.

These observations are consistent with the following kinetic scheme:

$$Ar_2CROH + H^+ \rightleftharpoons Ar_2CR\overset{+}{O}H_2 \tag{1}$$

$$Ar_2CR\overset{+}{O}H_2 \rightleftharpoons Ar_2\overset{+}{C}R + H_2O \quad \text{fast} \tag{2}$$

$$Ar_2CROH \rightleftharpoons Ar_2\overset{+}{C}R + OH^- \quad \text{very slow} \tag{3}$$

In acetic acid, step (1) is rapid because the reactants are moderately concentrated, but in catechol/catecholate solution, the hydrogen ion concentration is so low ($\sim 10^{-9} M$) that step (1) is slow and results in slow development of color[17] even though step (2) is rapid. Step (3) would be very slow in any case because OH^- is a poor leaving group[18]. Iodine could catalyze the dissociation by a mechanism like steps (4) to (7):

$$Ar_2CROH + I_2 \rightleftharpoons Ar_2RCO\overset{H}{\underset{I-I}{\diagdown}} \quad \text{fast} \tag{4}$$

$$Ar_2RCO\diagdown{}^{\diagup H}_{\diagdown I-I} \rightleftharpoons Ar_2R\overset{+}{C}O\diagdown{}^{\diagup H}_{\diagdown I} + I^- \quad \text{fast} \tag{5}$$

$$Ar_2R\overset{+}{C}O\diagdown{}^{\diagup H}_{\diagdown I} \rightleftharpoons Ar_2\overset{+}{C}R + HOI \quad \text{fast} \tag{6}$$

$$HA + HOI + I^- \rightleftharpoons H_2O + I_2 + A^- \quad \text{fast} \tag{7}$$

Iodide ion is known to be a good leaving group[18], and HOI would be expected to be a good leaving group because HOH is. Thus steps (5) and (6) should be rapid. The $Ar_2CROH \cdot I_2$ complex might resemble the well-known charge-transfer complexes of ethanol[19,20] and ethers[21] with iodine. Excitation of this complex (e.g., by light or thermally) might lead to a dissociation in which steps (5) and (6) are simultaneous. A fast rate is assumed in step (7) for the sake of this hypothesis. If the acid HA is NH_4^+ or RNH_3^+, step (7) might be very slow (exchange of protons between NH_4^+ and H_2O is known to be slow from NMR studies)[22,23], and this could account for the ineffectiveness of I_2 catalysis in the color test with acids NH_4Cl or glycine.

ACKNOWLEDGEMENT

SUMMARY

Gilman's Color Test I has been modified in two different ways to enable it to detect aryl metallic compounds, even in the presence of metal alkyls, thus performing the function of Color Test III.

In modification Color Test IC, where the C denotes catechol, an active organometallic reagent RM is added to Michler's ketone ($Ar_2C=O$) as usual. Water is added to hydrolyze the addition product to Ar_2RCOH and is followed by 1–2 ml of 20% aqueous catechol, producing a buffered solution with a pH near 9. The trisubstituted methanol Ar_2RCOH dissociates to the colored carbonium ion only if R is aryl. If R is alkyl, no color develops. A colorless solution may be tested further for the presence of alkyl by adding a few drops of glacial acetic acid: the appearance of a color indicates the presence of an alkylmetallic reagent.

In modification Color Test IB, where the B denotes bisulfate, 1 ml of 20% aqueous solution of $NaHSO_4$ is added to the colored solution resulting from Gilman's Color Test I. The solution decolorizes for R = alkyl, but the color remains for R = aryl.

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