

against time and the initial rate estimated from the curve. With the same catalyst in acetic acid the values which were constant over most of the run were averaged.

Density measurements were made on the solvents, the catalyst and the sugar acetate in several solvents to aid in the calculation of solvent composition.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXIV. The Effect of Sodium Reagents on Indicators¹

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Organosodium reagents, potassium and sodium hydroxide, will cause indicators of the type of benzeneazodiphenylamine to change to the same color as is produced by strong acids. Water helps produce the color when *n*-butyllithium and ethylmagnesium bromide are used.

The behavior of indicators with alkali metal reagents, particularly solids, is interesting because the colors produced imply a *pH* value. Similar tests have already been applied by Walling² to copper sulfate, calcium chloride, magnesium perchlorate and other solids which show little chemical reactivity with organic compounds, and the color changes suggest acidity. Also measurements with indicators have been made of alumina-silica sur-

hydroxide and others, all as solids suspended in some medium or, where possible, dissolved in ether. As might be expected, these reagents cause trinitrobenzene, ethyl bis-(2,4-dinitrophenyl)-acetate, and *m*-nitrophenol to show color on the basic side. However, they also had the unique feature of producing at once the color which certifies acidity with benzeneazodiphenylamine and 2-amino-5-azotoluene.

TABLE I
COLORS INITIALLY PRODUCED ON VARIOUS INDICATORS BY ALKALI METAL REAGENTS

Indicators ^a <i>pH</i> Acid color ^b Basic color ^c	Sol. ^d *	I	II	III	IV	V	VI	VII
		1.2-2.9 Violet Yellow	Red-vio. Yellow	1.4-2.8 Red Yellow	2.8-4.4 Red Yellow	6.8-8.6 Colorless Yel.-or.	8-10 Colorless Blue	2-14 Colorless Red-br.
C ₆ H ₅ Na ^c	PP	V	V	R	d	O	d	R-B
C ₆ H ₅ Na	P	V						
(C ₆ H ₅) ₃ CNa	E	V	Y					
C ₁₃ H ₉ Na	P	V		R	N	R	C	C
C ₁₃ H ₉ Na	E	V	Y	R	N	R	Bl	Bl
(CH ₃) ₃ CONa	T	Y	Y	Y	Y			
(CH ₃) ₂ CHOK	P	Y	Y	Y	Y			
KOH (t)	P	V	N	R	N	Y-O	B	R
KOH (t)	B	V		R	N	O	B	R
KOH (t)	E	R-V		Y	N	O	B	R
KOH (t)	W	Y		Y	Y	O	B	R
KOH (p)	P	V	N	R	N	Y-O	B-Bl	R
NaOH (t)	P	V						
NaOH (p)	P	Y		Y	N	O-R	B	R-B
LiOH	P	Y		Y	Y	O	B	R
B(OH) ₂	P	Y		Y	Y	Y	B	C
NaCl	P	N		N	N	N	N	N

^a In the order of numbering the indicators are benzeneazodiphenylamine, *p*-(phenylmethylamino)-azobenzene, 3,2¹-dimethyl-4-aminoazobenzene, *p*-dimethylaminoazobenzene, *m*-nitrophenol, ethyl bis-(2,4-dinitrophenyl)-acetate and 1,3,5-trinitrobenzene. ^b The abbreviations used for the colors are obvious from the colors listed for acid and base. Bl means black. In addition, "d" indicates the solution and solid reagent were decolorized, "N" means no absorption occurred. ^c For the hydrocarbon residues, C₆H₅, C₆H₅ and C₁₃H₉ refer, respectively, to allyl, phenyl and fluorenyl. The letters "c," "t," and "p" in parentheses, after some formulas, refer, respectively, to catalyst (Alfin), technical grade and prepared from the metal and water in pentane suspension. ^d The abbreviation for solvents are the first letters for pentane, ether, toluene, benzene and water.

faces.^{2,3} The present study consists of tests with a wide range of indicators on representative sodium reagents, an Alfin catalyst, triphenylmethylsodium, 9-fluorenylsodium, potassium hydroxide, sodium

Table I lists the results from test-tube experiments. The first and third indicators have the general structure RN=NR'NHR" where R and R' are aromatic nuclei and R" is hydrogen or phenyl. All organosodium reagents, solid potassium hydroxide and the commercial solid sodium hydroxide (but not one prepared from sodium and water suspended in pentane) caused the acid color

(1) The authors are indebted to the Office of Synthetic Rubber, Reconstruction Finance Corporation, for financial support of this work.

(2) C. Walling, *THIS JOURNAL*, **73**, 1164 (1950).

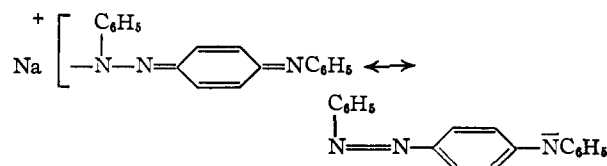
(3) M. W. Tamele, *Far. Soc., Discussions No. 8*, 270 (1950); T. H. Milliken, Jr., G. A. Mills and A. G. Obiad, *ibid.*, 279 (1950).

of these two indicators to appear. Lithium hydroxide, potassium isopropoxide, sodium chloride and sodium isopropoxide with sodium chloride (two components of the Alfin catalyst), all as solids, and sodium *t*-butoxide in toluene solution caused no color change. The acid colors on the Alfin catalyst and potassium hydroxide persisted overnight. With the other reagents the color disappeared within a very short time, possibly because air or moisture reacted with the reagents. On the other hand, moisture or other impurity may sometimes have a role in the formation of the color because commercial caustic soda caused the acid color to form while a sample freshly prepared from sodium and water did not and water helped to produce a color when butyllithium and ethylmagnesium bromide were used. In Walling's tests² a little water at times affected the color.

No acid color formed with the second or fourth indicator which have no hydrogen on the nitrogen. The colors with the last three indicators were all on the basic side and show that no unusual behavior was found in these cases.

A color effect was not limited to azo indicators. With 9-fluorenylsodium, piperonalacetophenone turned slowly to a pink-red color approaching that produced by aluminum chloride. The color persisted for hours.

These tests prove that some indicators which commonly are used to detect acidity with very strong acids will give the acid color with alkali metal reagents, indeed, with reagents which are sometimes catalogued as unusually strong bases.⁴ This fact suggests caution where indicators are used outside of aqueous or acidic media where they were originally applied. As to the reason why an acid color appeared in such unusual environments, the first thought is to assume that the color is that of the conjugate base obtained by replacement of the hydrogen of the amine by the alkali metal ion. An anion benzeneazodiphenylamine would have the two structures below that would contribute to resonance. This idea is supported by the fact



that only those azo indicators which have a replaceable hydrogen⁵ have so far shown the acid color with sodium reagents. Furthermore some of the reagents tested are notably active in such

(4) F. C. Whitmore and H. D. Zook, *THIS JOURNAL*, **64**, 1783 (1942); J. D. Roberts and D. Y. Curtin, *ibid.*, **68**, 1658 (1946).

(5) When Dr. Walling's attention was called to this work, he carried out tests of the following indicators on solid potassium hydroxide ground under a hydrocarbon solvent. The authors are greatly indebted to him for permission to include these results.

Indicator	Solvent	Color
$\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$	Pet. ether	Vio.
$\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$	Benzene	Blue
$p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$	Benzene	Red-br.
$[p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4]_2$	Benzene	Yellow
$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5$	Pet. ether	No ads. Y
$\text{C}_6\text{H}_5\text{CO}_2\text{C}_6\text{H}_4\text{-1,4-(NHC}_6\text{H}_5)_2$	Pet. ether	No ads. Bl

replacement reactions. The instant formation of color is, however, most unusual in an ordinary replacement reaction, particularly with such weak reagents as sodium and potassium hydroxides and the need for water in a few cases is not explained thereby. The formation of a complex may accordingly play a role.

Experiments

The Sodium and Potassium Reagents.—Allylsodium was made by cleavage⁶ of 29.4 g. (0.3 mole) of diallyl ether by 13.8 g. (0.6 g. atom) of sodium in 600 ml. of pentane in the high-speed stirring apparatus.⁷

The Alfin catalysts were made by two methods. The first was from 0.6 mole of amyl chloride, 0.3 mole of sodium and 0.5 mole of sodium isopropoxide, according to the method⁸ used extensively in this work. Ordinarily these preparations have a deep blue color—the conventional blue from a Wurtz reaction—but the one chosen for these tests had faded, on standing for nine months, to gray with a light blue cast. The second method was by cleavage of diallyl ether, 29.4 g. (0.3 mole) with 13.8 g. of sodium in the presence of 0.3 mole of sodium isopropoxide and 0.4 mole of sodium chloride, according to a method which will be described in more detail in a later publication.⁶

Triphenylmethylsodium was made⁹ from triphenylchloromethane and sodium amalgam.

9-Fluorenylsodium was made by metalation¹⁰ of fluorene with amylsodium. Ether was added to the suspension in order to dissolve some of the compound.

Merck and Co., Inc., potassium and sodium hydroxide pellets were used for the commercial caustics. A single pellet was usually ground in an agate mortar under dry (over sodium) pentane, benzene or ether for each test. The powder and some of the solvent were then transferred to the test-tube.

These caustic alkalies were also prepared by the dropwise addition of water to a slight excess of sodium or potassium sand suspended in pentane in the high-speed stirring apparatus under an atmosphere of dry nitrogen.

The isopropoxide and *t*-butoxide salts were made similarly from the alcohol and metal in the solvent listed in Table I.

Tests with Indicators.—The azo indicators were in the main obtained from Eastman Kodak Company but for the tests with lithium and Grignard reagents the indicators were synthesized in order to obtain pure materials. For the test-tube experiments, solutions of about 10 mg. of each indicator per 100 ml. of pentane, benzene or ether were prepared. For nearly all tests the active sodium reagents were first pipetted into a small (10 × 75 mm.) test-tube. The transfer to the pipet was made by pushing the suspension or solution up into the pipet by nitrogen pressure. Ordinary care was taken to have the test-tube dry and filled with nitrogen. The tube was stoppered with a cork immediately after transfer. With potassium or sodium hydroxide powders the transfer to the test-tube was made with a spatula and nitrogen was not used. The indicator was added with a dropping funnel. Appropriate color comparison tubes were made with boron trifluoride etherate, and magnesium perchlorate for the azo indicators and with strong aqueous solutions of the caustic alkalies for the base indicators. To the eye the colors obtained in the tests with the alkali metal reagents were identical with the corresponding standards.

With the Alfin catalyst and allylsodium the color with the first, third, fifth and eighth indicators faded, sometimes very rapidly. The color obtained with triphenylmethylsodium and indicator I faded in the test-tube but seemed permanent in a flask well protected from air and moisture. The acid colors produced by potassium hydroxide in pentane lasted overnight and longer, but in benzene the color produced with indicator No. III was fleeting.

(6) A. A. Morton, F. H. Bolton, F. W. Collins and E. F. Cluff, *Ind. Eng. Chem.*, **44**, 2876 (1952).

(7) A. A. Morton and L. S. Redman, *ibid.*, **40**, 1190 (1948).

(8) A. A. Morton, R. P. Welcher, F. Collins, S. E. Penner and R. D. Coombs, *THIS JOURNAL*, **71**, 481 (1949).

(9) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 607.

(10) A. A. Morton and E. L. Little, Jr., *THIS JOURNAL*, **71**, 487 (1949).

Removal of the Indicator.—Triethylamine (Eastman Kodak Company) was dried over potassium hydroxide pellets and freed from any secondary amine by two fractionations. The amine was added dropwise to the test-tube which contained the benzeneazodiphenylamine indicator absorbed on the Alfin catalyst or potassium hydroxide. The color was removed completely from the solid. The order of addition was reversed by adding the amine to the suspension, then adding the indicator solution whereupon no color developed. Triethylamine also removed the colors produced from 9-fluorenylsodium by this azo indicator or the piperonalacetophenone indicator.

The removal of color with the unsaturated hydrocarbons was tested similarly except that propylene was bubbled through the suspension. Before use the isoprene and 2,3-dimethylbutadiene were freshly distilled. The propylene (Phillip's Pure Grade) was dried by passage through two tubes of Drierite and two bottles of a pentane suspension of amylsodium.

Reaction with *n*-Butyllithium.—The reagent was prepared from 1.5 g. of lithium and 9.25 g. of *n*-butyl chloride in 100 ml. of ether in a 200-ml. creased flask with gentle stirring.

For the reaction with the indicator a 200-ml. flask already attached to the stirrer was heated by a Glas-col heater while a stream of dry nitrogen was passed through in order to remove air and moisture. The flask was then cooled in dry nitrogen. Anhydrous ether (25 ml.) was added, followed by 25 ml. of the ethereal *n*-butyllithium solution (17 millimoles of reagent). The stirrer was started slowly and a solution of 0.135 g. (0.495 millimole) of benzeneazodiphenylamine in 25 ml. of anhydrous ether was added dropwise. As each drop of the indicator was added a red-violet color formed momentarily, then gave way to a yellow. When all

of the indicator had been added, the solution was yellow and no precipitate was present. Water was then added slowly and cautiously. Within a short time the violet color reappeared. Eventually the addition of enough water to destroy the lithium reagent caused the violet color to be replaced by the original yellow of the indicator solution.

Reaction with Ethylmagnesium Bromide.—A practically identical test was carried out between 5 ml. of an ethereal solution which contained 5.36 millimoles of ethylmagnesium bromide added to 366 mg. (1.34 millimoles) of benzeneazodiphenylamine in 25 ml. over a period of five minutes. Again no violet color appeared but the addition of more water destroyed the color. From the ether layer 93% of benzeneazodiphenylamine, which melted at 81.5–84°, was recovered. The recorded¹¹ value is 82.5 and the sample, as prepared¹² in this Laboratory, melted at 83°.

A similar test was carried out between 5.36 millimoles of ethylmagnesium bromide and 366 mg. of *p*-(phenylmethylamino)-azobenzene. No acid color developed when the reagents were mixed but the addition of a few drops of water produced the characteristic red-violet color. More water was added to destroy the color. Evaporation of the ether layer gave a 90% recovery of the azo compound which melted at 73–75°. The compound, as prepared by coupling diazotized aniline with methyldiphenylamine, melted at 75–76°.

Anal. Calcd. for C₁₉H₁₇N₃: N, 14.6. Found: N, 14.35.

(11) L. P. Hammett and M. A. Paul, *THIS JOURNAL*, **56**, 827 (1934).

(12) H. A. Torrey and W. MacPherson, *ibid.*, **31**, 582 (1909).

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Applications of the Hunsdiecker Silver Salt Degradation. The Preparation of Dibromides and Tribromides¹

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The Hunsdiecker degradation has been successfully applied to an α -bromo acid, to a β -bromo acid, to a substituted malonic acid, to succinic acid and, in poor yield, to a tricarboxylic acid. Portionwise addition of silver salt to the bromine solution and maintenance of low temperature are conditions favorable to the reaction.

For the preparation of polybromides by the Hunsdiecker silver salt degradation,² three types of starting materials are to be considered: polycarboxylic acids, bromo acids and unsaturated acids. Although numerous dicarboxylic acids have been studied,³ apparently no attempt has been made to utilize a tricarboxylic or higher polycarboxylic acid in this way. As regards bromo acids, a search of the literature discloses only the patented conversion^{3b} of α -bromostearic acid to 1,1-dibromoheptadecane and the recent prepara-

tion⁴ of pentabromoheptadecane from tetrabromostearic acid. There is no report of the successful direct application of the Hunsdiecker reaction to an unsaturated acid.

In the present research two experiments with unsaturated acids were carried out. Silver allylacetate, added to a refluxing solution of bromine in carbon tetrachloride, gave bromolactone, and silver methacrylate, added to a bromine solution at 0° yielded polymer; in neither case was the production of carbon dioxide noted.

In reactions involving the silver salt of a bromo acid, a limiting factor is obviously the stability of the salt. The silver salts of α -bromovaleric acid, β -bromopropionic acid and δ -bromovaleric acid⁵ were found to be stable at 0° but to decompose⁶

(4) D. R. Howton, R. H. Davis and J. C. Nevenzel, *ibid.*, **74**, 1109 (1952).

(5) Prepared in good yield by addition to allylacetic acid of hydrogen bromide in toluene at 0° in the presence of benzoyl peroxide. After vacuum distillation and recrystallization from ligroin, the acid melted at 39–40°.

(6) Silver β -bromopropionate, on drying *in vacuo* at room temperature, gave β -propiolactone identified as β -isothioureidopropionic acid, m.p. 178–179°; cf. T. L. Gresham, J. E. Jansen and F. W. Shaver, *THIS JOURNAL*, **70**, 998 (1946).

(1) This research received support from the Research Corporation and from the Office of Naval Research.

(2) See J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947); C. F. H. Allen and C. V. Wilson, *Org. Syntheses*, **26**, 52 (1946).

(3) (a) W. Bockemüller and F. W. Hoffmann, *Ann.*, **519**, 165 (1935); (b) C. Hunsdiecker, H. Hunsdiecker and E. Vogt, French Patent 803,941; British Patent 456,565; German Patent 695,062 [C. A., **31**, 2233 (1937); *Chem. Zentr.*, **108I**, 2258 (1937)]; H. Hunsdiecker, C. Hunsdiecker and E. Vogt, U. S. Patent 2,176,181 [C. A., **34**, 1685 (1940)]; (c) A. Lüttringhaus and D. Schade, *Ber.*, **74**, 1565 (1941); (d) V. Prelog and R. Seiwert, *ibid.*, **74**, 1769 (1941); (e) K. Ziegler, C. Schenck and E. W. Krockow, *Naturwiss.*, **29**, 390 (1941); *Ann.*, **551**, 1 (1942); (f) H. Hunsdiecker and C. Hunsdiecker, *Ber.*, **75**, 291 (1942); (g) H. Schmid, *Helv. Chim. Acta*, **27**, 127 (1944); (h) J. W. H. Oldham, *J. Chem. Soc.*, 100 (1950); (i) M. Hauptschein, C. S. Stokes and A. V. Grosse, *THIS JOURNAL*, **74**, 848 (1952).