

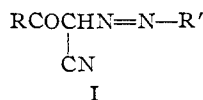
prepared from cobaltammines and halogenostannic acids, and a novel form of metastannic acid has been obtained by the hydrolysis of these compounds. PHILADELPHIA, PENNA. RECEIVED NOVEMBER 29, 1946

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

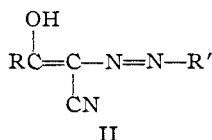
Chromium Complexes of Azo Dyes Derived from Acylacetonitriles¹

BY ROBERT S. LONG

This work was initiated to determine whether azo dyes of type I, derived from acylacetonitriles and certain specific types of diazo compounds to be described later, could be converted to stable chromium complexes.



Certain types of active methylene compounds such as β -diketones and β -ketoesters had been used for this purpose, but there was no record of the use of β -cyanoketones. Although several of the acylacetonitriles recorded in the literature had been reported to be alkali-soluble and to couple with diazo compounds, it was not certain whether the activating effect of the cyano group on the methylene group would be sufficient to promote enolization in the azo dye (I) to give the enolic form (II) believed necessary for metallization.



The presence of a metallizable group in ortho position at each end of the azo linkage has been shown to be necessary for the formation of stable metal complexes. This necessitates the use of an *o*-aminophenol or an anthranilic acid derivative as the diazo component if the azo dye is to be metallized by simple procedures. The diazo compounds derived from anthranilic acid and its derivatives are fairly active couplers, but the diazo compounds derived from *o*-aminophenols are very weak couplers—much weaker than the corresponding diazo compounds without the hydroxyl group. The coupling of acetoacetonitrile with diazo sulfanilic acid² and of several aromatic acylacetonitriles with various diazo compounds³ has been reported previously. However, none of the diazo compounds used contained an hydroxyl or carboxyl group ortho to the diazo group.

(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Chicago, Ill., Sept. 13, 1946. A portion of this work has also appeared in U. S. Patents 2,366,633 and 2,392,167 (Long to American Cyanamid Company).

(2) Justoni, *Gazz. chim. ital.*, **70**, 804-812 (1940); *C. A.*, **35**, 5110 (1941).

(3) McNally and Dickey, U. S. Patent 2,211,339 (1940).

Preparation of the Chromium Complexes.—A number of acylacetonitriles have now been prepared, many of them new compounds. They have been found to couple readily with diazo compounds containing hydroxyl and carboxyl groups ortho to the diazo group. The dyes described in this paper were mostly prepared by coupling in aqueous sodium hydroxide solution, but the coupling may also be carried out, in most cases equally satisfactorily, in sodium carbonate solution, although the reaction is somewhat slower.

The azo dyes were found to be easily converted to the corresponding chromium complexes. The procedure consists of refluxing the dye in water solution with a small excess of basic chromic acetate. A rapid conversion to partially metallized dye takes place as evidenced by complete solution of the dye and a marked deepening in the color of the solution. When the pH is lowered to the range 1-4 and refluxing is continued, a gradual conversion takes place to the fully metallized dye containing one atom of chromium per molecule of dye. Usually this complex is much less soluble and precipitates from the reaction mixture in a well-defined crystalline form.

The over-all yield for the coupling and metallization is usually at least 80% of theory under optimum conditions. In a number of the examples reported in this paper the yield is lower because it varies considerably with small changes in pH and concentration of the metallization and no effort has been made as yet to determine the optimum conditions for the preparation of most of these complexes.

The structure of the chromium complexes of azo dyes has not been studied extensively and the correct structure has not been established. The complex which is generally the most stable and the one most easily isolated contains one atom of chromium combined with one molecule of dye, based on the analytical data. This is the type of complex dealt with in this paper. It is also apparent from the analytical data that the complexes must contain an appreciable amount of water which is not removed by drying at 60°. The amount of water seems to vary from one complex to another.

Since the conversion to this complex often requires refluxing the dye in aqueous solution of pH 1-4 for as long as twenty-four hours, it is particularly gratifying that no decomposition of

the azo dyes takes place. The cyano group and the active methylene group in the acylacetonitrile both represent likely points for decomposition to set in. In fact, the acylacetonitrile is not stable to prolonged boiling under these conditions. Moreover, the azo dye derived from diazo 1-amino-2-hydroxynaphthalene-4-sulfonic acid and acetoacetanilide, although readily converted to a partially chromed dye, is decomposed when the pH is lowered and refluxing continued in an effort to form the completely chromed dye. That no decomposition takes place when the dyes from these acylacetonitriles are metallized is shown by the chromium/nitrogen ratio in the product.

Effect of Chromium and of Substituents on the Color.—It is interesting to compare the dyeing properties of the unmetallized dyes with those of the corresponding chromium complexes. The unmetallized dyes obtained from the acylacetonitriles described in this paper in many cases have practically no color value when applied to wool as acid dyes whereas strong bright dyeings are obtained in every case using the corresponding chromium complexes. In the cases where no appreciable color is obtained on the wool using the unmetallized dye, it seems probable that the dye decomposes during the boiling in the dye-bath. If this is the case, introduction of chromium must stabilize the molecule, since a strong dyeing is generally obtained by the meta-chrome method and there is no evidence of decomposition when the isolated chromium complex is used.

The nature of the diazo component and of the acylacetonitrile has a marked influence on the amount of color obtained from the acid and top-chrome dyeings. Thus, the only cases in which the acid dyes derived from an aminonaphthalene give any appreciable color when dyed on wool are those in which the radical R (formula I) contains a substituent other than hydrogen ortho to the —COCHCN radical. The shades of the acid dyes and the corresponding chromium complexes derived from 1-amino-2-hydroxynaphthalene-4-sulfonic acid and various acylacetonitriles are compared in Table II.

On the contrary, when R' is a substituted phenyl instead of a naphthyl radical the acid dye gives a much stronger dyeing, indicating an increased stability of the dye molecule. This is shown in Table III.

The effect of substituents in the aryl portion of the acylacetonitrile on the shade of the dyeing from the chromium complex is also apparent from Table II. Thus, a marked deepening or "blueing" of the shade is caused by the introduction of negative groups such as halogen, nitro and carboxyl. A similar effect is obtained by substitution of a heterocyclic or fused ring system for the benzene ring. On the other hand, yellower shades are obtained by the introduction of alkyl and alkoxy groups or by hydrogenation of the benzene ring.

Fortunately, the dyeings, as well as usually being bright, attractive shades, are characterized also by excellent fastness to washing and light with only the latter exhibiting an appreciable variation. The dyes derived from heterocyclic acylacetonitriles or from acylacetonitriles containing negative substituents in the acyl radical tend to be somewhat less fast to light but the difference is not great.

Preparation of the Acylacetonitriles.—Various methods of preparation of the acylacetonitriles were examined in an effort to find the method which would permit their preparation most efficiently. Methods reported previously include reaction of the α -halogen ketone with sodium or potassium cyanide (numerous references), reaction of cyanoacetyl chloride with aromatic hydrocarbons in the presence of aluminum chloride,⁴ reaction of benzoylacetalddehyde with hydroxylamine in alkaline solution⁵ and reaction of ethyl benzoate with acetonitrile in the presence of sodium ethoxide.⁶

Several of the compounds reported in this paper were prepared by the cyanide method but this method is not very satisfactory as a general method of preparation. The α -chloroketones are lachrymators and usually difficult to handle, and the reaction with cyanide tends to give an impure product unless the cyanoketone is highly insoluble and precipitates from the reaction mixture as formed.

The second method using cyanoacetyl chloride would appear to be a convenient and direct method of obtaining many compounds of this type. However, it was not investigated because of the instability of cyanoacetyl chloride and the success obtained with the acetonitrile method.

The preparation by way of the oxime was tried only in the case of *p*-chlorobenzoylacetonitrile. Oximes of this type dehydrate readily in alkaline solution but the yield is low in both this step and in the condensation of the methyl ketone with methyl formate.

The method of Dorsch and McElvain appears to have been used only by them and the only acetonitrile condensation which they carried out was with ethyl benzoate. This method has now been applied to a large variety of compounds and found to be extremely valuable when the ester is readily available. It has been found that commercial sodium methoxide may be used and that the ester, acetonitrile and sodium methoxide may be mixed at room temperature and then stirred and heated until the reaction is complete. In some cases the reaction mixture solidifies before the reaction is complete and a low yield results, but this may be avoided by the use of an inert solvent such as chlorobenzene which permits efficient stirring. The only appreciable by-product is the acid corresponding to the ester used and

(4) Eckert, Sieber and Greune, U. S. Patent 1,972,219.

(5) Claisen and Stock, *Ber.*, **24**, 130 (1891).

(6) Dorsch and McElvain, *THIS JOURNAL*, **54**, 2960 (1932).

this is easily removed by taking advantage of its greater acidity. Most of the yields reported in this paper represent minimum yields and could undoubtedly be improved by variation of the amount of solvent and/or reaction temperature. The method does not appear to be useful for compounds containing acidic groups because of reaction with the sodium methoxide giving a very insoluble sodium salt which does not react further. It is also not useful with esters which contain substituents which react with the sodium methoxide.

The by-product carboxylic acid obtained seems to be formed partially because of the presence of small amounts of sodium hydroxide and sodium carbonate in the commercial sodium methoxide. However, the amount formed is usually larger than would be expected from these impurities. This additional acid is probably formed by reaction of sodium methoxide with the methyl ester to form dimethyl ether and the sodium salt of the acid.

Acknowledgment.—I should like to express my appreciation to Miss Abby Nies who carried out much of the laboratory development work and to Doctor Glen Watson who has been largely responsible for the successful technical development of certain of these products.

Experimental⁷

Preparation of Acylacetoneitriles

Method I.—The general procedure which was used for the preparation of most of these compounds is that described by Dorsch and McElvain.⁶ Modifications which were made include the use of commercial sodium methoxide instead of sodium ethoxide, mixing of the methyl ester, sodium methoxide and acetonitrile at room temperature, and, in certain cases, the use of an inert solvent such as chlorobenzene or *o*-dichlorobenzene to permit more efficient stirring. The reaction mixture was usually heated overnight in an oil-bath at 90–100°. After completion of the reaction, the mixture is cooled and treated with water (usually 100 cc. for 0.1 mole) to give a solution of the sodium salt of the product. Unreacted ester is removed by clarification with Darco or by ether extraction if the amount is large. Acidification to pH 6 precipitates the nitrile in sufficiently pure form for use in the coupling reaction. The only appreciable byproduct is the carboxylic acid corresponding to the ester used, and this may be recovered by further acidification of the filtrate to pH 2 or less. It is probable that in most cases the yield shown in the table does not represent a maximum yield since the reaction was usually only carried out once.

New products were purified for analysis by crystallization from a solvent as noted, but the crude product from the reaction mixture was usually sufficiently pure for the coupling reaction. Physical and analytical data of all the compounds prepared are given in Table I. Included also in the table are several compounds which were prepared by different procedures as described below. No attempt was made to purify previously reported compounds completely.

Method II.—This procedure is similar to that reported previously for the preparation of benzoylacetoneitrile.⁶ The preparation of 4-chlorobenzoylacetoneitrile, the only compound prepared by this method, is described in detail since several modifications were made.

4-Chlorobenzoylacetoneitrile was prepared by the dropwise addition of a mixture of 6.0 g. (0.1 mole) of methyl

formate and 15.5 g. (0.1 mole) of 4-chloroacetophenone to a cooled suspension of 5.7 g. (0.1 mole) of 95% commercial sodium methoxide in 100 cc. of dry toluene. The ice bath was then removed and in about ten minutes the sodium salt of the product separated as a thick, white precipitate. Absolute methyl alcohol (30 cc.) was added to facilitate stirring and the reaction mixture was stirred overnight at room temperature. The product was removed by filtration and dried at 60° giving 12.9 g. (56.3%).

To a suspension of 4.1 g. (0.02 mole) of this sodium salt in 20 cc. of water and 4 cc. (0.02 mole) of 5 *N* sodium hydroxide was added 1.5 g. (0.02 mole) of hydroxylamine hydrochloride dissolved in 5 cc. of water. The reaction mixture was then heated slowly to 80° and held at that temperature for one hour. The clear, yellow solution which resulted was diluted with 40 cc. of water and the small amount of yellow-orange oil which separated was removed by extraction with ether and discarded. Acidification of the alkaline solution gave 1.7 g. (47.2%) of 4-chlorobenzoylacetoneitrile as a light orange solid, m. p. 115–123°.

Method III.—Reaction of the α -chloro ketone with sodium cyanide in aqueous alcohol. The general procedure consisted of dissolving or slurring the chloro compound in alcohol and adding an aqueous solution containing 3 mole equivalents of sodium cyanide at room temperature. The reaction is usually slightly exothermic so the cyanide should be added slowly. When the reaction is complete, water is added, the solution is clarified to remove insoluble material, and the nitrile is precipitated from the filtrate by acidification. For best results, the solution should be rendered only weakly acidic, preferably with acetic acid. The yield is nearly quantitative with compounds which precipitate as formed but is only 50–70% with more soluble compounds such as 4-methylbenzoylacetoneitrile, apparently because the higher solubility in the reaction medium favors side reactions.

Method IV.—Nitration of benzoylacetoneitrile. This nitration was carried out by the gradual addition of 14.5 g. of benzoylacetoneitrile to 50 cc. of 96% nitric acid. The nitric acid was cooled in an ice-bath and the addition was carried out at such a rate that the temperature did not rise above 10°. Stirring was continued for five minutes and the solution was then poured into 250 cc. of ice and water. The white precipitate (m. p. 112–140°) which separated was recrystallized from 200 cc. of ethyl alcohol giving 7.3 g. (38%); m. p. 146–148°.

Method V.—Catalytic reduction of the corresponding nitro compound in alcohol with Raney nickel catalyst.⁹

Preparation of Dyes and Chromium Complexes

Preparation of Azo Dyes from 1-Amino-2-hydroxynaphthalene-4-sulfonic Acid and Acylacetoneitriles.—The general procedure used for this coupling reaction is as follows:

The acylacetoneitrile (1 mole equivalent plus 5% excess) was dissolved in water (about 200 cc. or 0.1 mole) with the aid of 2–3 mole equivalents of sodium hydroxide. To this solution was added a solution of an equivalent amount of the diazo compound derived from 1-amino-2-hydroxynaphthalene-4-sulfonic acid in water (about 100 cc. for 0.1 mole) and one equivalent of sodium hydroxide. The solution became deeply colored rapidly but the reaction did not reach completion until the reaction mixture had been stirred for a number of hours (usually overnight) at room temperature. The reaction was followed by spotting a sample of the coupling solution on filter paper against a solution of resorcinol in dilute ammonia. A deep violet color forms at the meeting point of the two spots as long as any diazo compound is present. The reaction mixture was then diluted with about an equal volume of water and the azo dye isolated by acidification with mineral acid. The product was removed by filtration, washed with water and dried at 50–60°. The yield was usually more than theory because it is very difficult to wash all of the salt out of the dye without dissolving the dye. The purity of the azo dye may be determined by titration of the azo linkage with titanium trichloride. This was

(7) All melting points are corrected. Micro analyses carried out under the direction of Mr. O. E. Sundberg.

TABLE I
 ACYLACETONITRILES, RCOCH₂CN

R =	M. p., °C.	Prepn.	Yield, %	Crys. solv. ^a	Analyses, %					
					Calcd.			Found		
					C	H	N	C	H	N
Phenyl	80-81 ^b	I	70							
4-Chlorophenyl	125-129 ^c	II	25	B-PE	60.2	3.34	7.80	59.8	3.64	7.99
3,4-Dichlorophenyl	105-107 ^d	I	25	E	50.5	2.34		50.5	2.30	
4-Methylphenyl	94-99 ^e	III	67							
2-Methoxyphenyl	87-88 ^f	I	65	E	68.6	5.14	8.00	68.4	4.81	8.25
4-Methoxyphenyl	126-129 ^g	I	30							
2-Ethoxyphenyl	121-122	I	70	E	69.8	5.83	7.40	69.6	5.58	7.97
2-Propyloxyphenyl	99-101	I	30	E	70.9	6.40	6.90	70.4	6.04	7.08
2-Benzyloxyphenyl	94-96	I	25	E	76.4	5.20	5.60	76.1	5.07	5.95
2,4-Dimethoxyphenyl	150-151 ^h	I	50	M	Not analyzed					
3,4,5-Trimethoxyphenyl	139-140 ⁱ	I	55	M	61.3	5.50	6.00	61.3	5.32	6.20
3,4,5-Triethoxyphenyl	118-119	I	40	75% M	65.0	6.88	5.06	64.9	6.60	5.09
3-Nitrophenyl	147-149 ^j	IV	40	E	56.8	3.16	14.8	56.1	3.22	14.7
3-Aminophenyl	102-109 ^k	V	56	E			17.5			16.9
3-Carboxyphenyl	174-176 ^l (dec.)	I	50	E-B	63.5	3.70	7.40	64.1	3.50	8.02
4-Carboxyphenyl ^m	230-231 (dec.)	I	10	M	Neut. equiv. calcd.: 189.			Found: 208		
4-(4'-Cyanoacetophenyl)-phenyl	Above 230 ⁿ	III	98	DCB	63.5	3.70	7.40	64.1	3.85	7.58
2-Phenylethenyl	96-98	I	..	M	75.0	4.20	9.70	74.0	4.03	8.72
Hexahydrophenyl ^o	B. p. 128 (5 mm.)	I	40				8.19			8.23
α-Naphthyl	96-97.5 ^p	I	70	E	71.5	8.61	9.27	71.1	8.33	9.30
β-Naphthyl	124-125 ^q	I	80		80.0	4.62	7.18	79.1	4.31	7.44
2-(5,6,7,8-Tetrahydronaphthyl)	95-96 ^r	III	50	60% E	Not analyzed					
3-Methoxy-2-naphthyl	150-151 ⁿ	I	64	B	74.7	4.90	6.20	74.8	4.84	6.45
5-Acenaphthyl	154-159 ^r	III	..	E						
2-Furyl	78-79 ^s	I	31	E	62.2	3.70	10.3	62.0	3.76	10.4
2-Thienyl ^t	131-135 ^u	I	50	E						

^a B, benzene; PE, petroleum ether (b. p. 30-60°); E, ethanol; M, methanol; DCB, *o*-dichlorobenzene. ^b Reported m. p. 80-81°. ^c Reported m. p. 129.5-130°. ^d Reported m. p. 105-107°. ^e Reported m. p. 104.6-105.2°. ^f Reported m. p. 87°. ^g Reported m. p. 128-130°. ^h Reported m. p. 149-151°. ⁱ Reported m. p. 138-139°. ^j Reported m. p. 152-153°. ^k This compound was very difficult to purify. It was completely soluble in dilute hydrochloric acid. Reported m. p. 87-95°. ^l Obtained by reaction of dimethyl *i*-phthalate with two moles of acetonitrile and sodium methoxide. Reported m. p. 170-175° (dec.). ^m Isolated as a by-product from the reaction of dimethyl terephthalate with two moles of acetonitrile and sodium methoxide. ⁿ Reported previously⁹ but no m. p. given. ^o Changes to a resinous material on standing. ^p Reported m. p. 96-97°. ^q Reported m. p. 127.6-128.2°. ^r Reported m. p. 169-171°. ^s Reported m. p. 79.5-80.5°. ^t Prepared by Dr. Corris Hofmann. ^u Reported m. p. 137°. ¹²

usually not done since the product was always of sufficient purity for the metallization reaction described below.

Preparation of the Chromium Complexes of Azo Dyes Derived from 1-Amino-2-hydroxynaphthalene-4-sulfonic Acid and Acetylacetonitriles.—The general procedure used for the preparation of the chromium complexes may be illustrated by the following example:

The dye (5.3 g.), from the coupling of 0.01 mole of the diazo compound derived from 1-amino-2-hydroxynaphthalene-4-sulfonic acid with a 5% excess of 3,4,5-triethoxybenzoylacetonitrile by the procedure described above, was placed in a flask with 50 cc. of water and 10 cc. of 1.1 *N* basic chromic acetate solution. The slurry was stirred and heated under reflux. The dye went into solution rapidly and a deep reddish purple solution was obtained. This stage signifies the formation of the soluble partially chromed complex. After refluxing for one hour, 25 cc. of water and 25 cc. of 1 *N* sulfuric acid were added. Refluxing was continued and within fifteen minutes a dark, crystalline solid started to separate. After two hours precipitation appeared complete, but refluxing was continued

for four hours longer. The product was removed by filtration from the hot solution, washed well with water and dried at 60°; yield, 4.7 g. (77.2% based on diazo compound used).

Since the exact formula of the chromium complex is not known, the chromium/dye ratio is determined by analysis for chromium and nitrogen.

Anal. Found: Cr, 8.80; N, 6.90; Cr/dye ratio, 1.03.

For the same reason the percentage yield is not calculated in the usual manner but is based on the nitrogen analysis. Thus, if the theoretical yield of complex containing three atoms of nitrogen is one mole, the theoretical amount of nitrogen present is 3.0 atoms, or 42 g.

The complexes prepared, yields and analytical data are given in Table II.

In most cases the formation of the insoluble, fully chromed dye is slower than in the above experiment, and refluxing was usually continued overnight. In a few cases, as noted in the table, it was necessary to cool the solution and add salt to precipitate the product.

Preparation of Chromium Complexes of Azo Dyes from Miscellaneous Diazo Components and Acylacetonitriles.—The necessary azo dyes were prepared by the general procedures reported previously.⁹ The amines used were either commercial materials or were prepared by conventional procedures. The metallizations were carried out by the general procedure given for dyes derived from 1-amino-2-hydroxynaphthalene-4-sulfonic acid. The yields

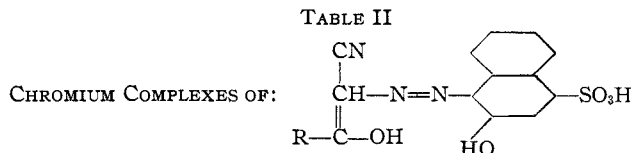
(8) Rabcewicz-Zubkowski and H. Kafinska, *Roczniki Chem.*, **10**, 541-568 (1930); *C. A.*, **25**, 505 (1931).

(9) Long, U. S. Patent 2,392,167.

(10) Sonn, *Ber.*, **51**, 825 (1918).

(11) German Patent 536,652 (*Frdl.*, **18**, 612 (1933)).

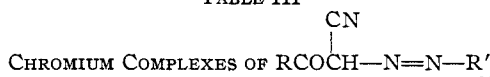
(12) Salvatori, *Gazz. chim. ital.*, **21**, II, 284 (1901) (*Beil.*, **18**, 408).



R =	Yield, % ^b	Analyses, % ^c found			Cr/dye ratio	Shade on wool ^a	
		Cr	N	Cr/dye ratio		Acid dye	Cr complex
Phenyl	44.7	8.66	6.96	1.06	Tan	Bordeaux	
4-Chlorophenyl	66.1	7.55	5.72	1.07	Buff	Blue-bordeaux	
3,4-Dichlorophenyl ^c	72.0	8.67	6.97	1.01	Buff	Very blue bordeaux	
4-Methylphenyl ^c	37.7	9.08	6.09	1.21	Buff	Bordeaux	
2-Methoxyphenyl ^c	75.2	9.50	7.89	0.98	Red-yellow	Yellow-bordeaux	
2-Ethoxyphenyl	68.6	8.96	7.79	.93		Yellow-bordeaux	
2-Propyloxyphenyl	38.1	9.59	7.27	1.07		Yellow-bordeaux	
2-Benzoyloxyphenyl	1.6 g.	Sample not anal.				Red-violet	
2,4-Dimethoxyphenyl	55.8	8.60	6.90	1.00		Yellow-bordeaux	
3,4,5-Trimethoxyphenyl	54.3	8.80	6.90	1.03	Tan	Very blue bordeaux	
3,4,5-Triethoxyphenyl	80.0	9.15	7.15	1.03		Very blue bordeaux	
3-Nitrophenyl ^{c,e}	31.0	4.85	5.43	0.96	Buff	Violet	
3-Aminophenyl ^c	28.0	7.02	6.09	1.25		Violet-brown	
3-Carboxyphenyl ^{c,f}	49.7	7.37	4.09	1.45	Buff	Violet	
4-(4'-Cyanoacetophenyl)-phenyl ^g	51.6	5.13	4.18	1.98 ^d	Buff	Violet	
Hexahydrophenyl	63.6	9.43	7.94	0.96		Red	
α -Naphthyl ^{c,h}	69.4	6.79	6.49	.85	Buff	Bordeaux	
β -Naphthyl ^c	65.3	8.28	6.82	.98	Orange-buff	Very blue bordeaux	
3-Methoxy-2-naphthyl	80.0	8.60	6.90	1.00	Red-yellow	Blue-bordeaux	
5,6,7,8-Tetrahydro-2-naphthyl	62.6	10.4	5.57	1.51 ^f	Buff	Blue-bordeaux	
5-Acenaphthenyl ^c	29.1	8.46	7.04	0.97	Orange-buff	Blue-bordeaux	
2-Furyl ^c	51.6	9.50	8.55	.90	Buff	Violet	
2-Thienyl ⁱ	57.5	9.04	7.91	.92		Violet	

^a A tan or buff shade indicates a weak dyeing. In general, the dyes which gave such shades gave similar, or slightly stronger, dyeings when after-chromed. Application of the unmetallized dye by the metachrome method usually gave a shade similar to that obtained from the chromium complex prepared in substance. ^b Calculated on the basis of the N analysis as explained elsewhere. ^c Reported previously.¹³ ^d Theory is 2.0; in all other cases 1.0. ^e Volume was 80 cc. Added 16 g. of salt. Product separated as an oil which solidified rapidly. ^f Volume was 100 cc. Added 20 g. of salt to obtain product. ^g Necessary to add 20 g. of salt to obtain product. ^h Obtained some product on cooling but added 30 g. of salt before filtering. ⁱ The product separated as an oil which solidified and in so doing probably adsorbed excess Cr salts. ^j Prepared by Dr. Corris Hofmann.

TABLE III



R =	R' =	Yield, % ^b	Analyses, % ^c found			Shade on wool ^a	
			Cr	N	Cr/dye ratio	Acid dye	Cr complex
3-Methoxy-2-naphthyl	2-Hydroxy-4-sulfo-6-nitronaphthyl	41	7.70	8.00	1.04	Red
3-Methoxy-2-naphthyl	2-Hydroxy-3-nitro-5-sulfo-phenyl	27	5.54	6.71	0.89	Yellow	Orange
α -Furyl	2-Hydroxy-4-sulfo-6-nitronaphthyl	66	7.40	9.70	0.82	Red
α -Furyl	2-Carboxy-4-sulfo-phenyl	13	8.70	5.90	1.19	Yellow
α -Furyl	2-Hydroxy-3-sulfo-5-chlorophenyl ^c	25	8.70	6.58	1.06	Yellow	Bordeaux
4,4'-Biphenylene	2-Carboxy-4-sulfo-phenyl	24	9.00	7.00	2.08	Yellow	Red-yellow
Phenyl	2-Hydroxy-4-sulfo-6-nitronaphthyl ^c	45	8.7	8.6	1.08	Buff ^d	Red
Phenyl	2-Hydroxy-5-sulfo-phenyl ^c	35	12.6	9.5	1.07	Yellow	Red
Phenyl	2-Hydroxy-4-sulfo-5-methylphenyl ^c	55	10.9	8.02	1.10	Yellow	Red
Phenyl	2-Hydroxy-3-sulfo-5-nitrophenyl ^c	50	10.6	9.5	1.20	Orange	Orange
Phenyl	2-Hydroxy-3-carboxy-5-sulfo-phenyl ^c	Not analyzed				Yellow	Yellow
Phenyl	2-Carboxy-4-sulfo-phenyl ^c	37	6.86	6.08	0.91	Yellow	Yellow
Phenyl	2-Hydroxy-3-sulfo-5-chlorophenyl ^c	36	10.1	8.10	1.01	Yellow-orange	Red

^a Unless noted to the contrary, these dyes gave shades by the topchrome and metachrome methods similar to the shades obtained from the chromium complex prepared in substance. ^b The yield represents the over-all yield for the coupling and metallization. ^c Reported previously.⁹ ^d The term "buff" is meant to indicate a weak dyeing. Similar results are obtained when the dye is applied by the topchrome method. The metachrome method gives a dyeing similar to that obtained from the chromium complex prepared in substance.

was not obtained. Yields, analytical data and results of dye tests are given in Table III.

Preparation of Intermediates.—Most of the methyl esters needed for the condensations with acetonitrile were obtained from the Eastman Kodak Company or were prepared by esterification of the corresponding acids by the conventional procedure. The derivatives of salicylic acid were found to be most readily prepared by etherification of methyl salicylate. The methyl and ethyl ethers were prepared using the corresponding dialkyl sulfates, the propyl derivative using propyl iodide, and the benzyl derivative using benzyl chloride.

The chloroacetyl derivatives of tetralin, acenaphthene, toluene and biphenyl were prepared by the conventional Friedel-Crafts reaction using chloroacetyl chloride.

Thiophene-2-carboxylic acid was prepared by oxidation of methyl 2-thienyl ketone by the procedure recommended for β -naphthoic acid.¹⁴

The necessary amines and diazo compounds were prepared by conventional procedures.

Methyl 3,4-Dichlorobenzoate.—This appears to be a new compound. It was prepared by esterification of 3,4-dichlorobenzoic acid by refluxing with methyl alcohol and a small amount of sulfuric acid. Recrystallization from methyl alcohol gave white crystals, m. p. 45–47° (cor.); yield, 78.4%. It was not analyzed.

Summary

The preparation of a new type of chromium

(14) "Organic Syntheses." Coll. Vol. II, p. 428.

complex of azo dyes is described. These azo dyes are derived from acylacetone nitriles and aromatic aminesulfonic acids containing hydroxyl or carboxyl groups ortho to the amino group. The complexes are stable either when dry or in aqueous solution. They have been shown to contain one atom of chromium for each molecule of azo dye.

The use of the unmetallized dyes as acid colors and chrome colors and of the chromium complexes as wool dyes is discussed with regard to the effect of the chromium and of substituents on the shade. In general, the chromium complexes have much more color value than the unmetallized dyes and the shade varies from yellow to violet depending on the nature of the acylacetone nitrile and the diazo component.

The method used by Dorsch and McElvain⁶ for the preparation of benzoylacetone nitrile has been shown to be applicable to the preparation of numerous acylacetone nitriles, not only in the benzene series but also in the naphthalene, furan and thiophene series.

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Aqueous Solubilities of Some Sulfamates, and the System Ammonium Sulfamate-Sulfamic Acid-Water at 25°¹

BY JOHN E. RICCI AND BERNARD SELIKSON

The technical uses and importance of sulfamic acid and its salts are increasing, but knowledge of the properties and solubilities of its inorganic salts is still rather scanty. Most of the published information on the preparation and properties of the pure acid and its salts, and on their solubilities in various solvents, is summarized in the articles of Cupery and Gordon² and in the review article by Audrieth and co-workers.³ This is a report of preliminary work beginning some systematic studies on the solubility relations of the simple sulfamates in aqueous systems.

I. Preparation and Properties of the Compounds.—

A. Sulfamic acid of sufficient purity was obtained by a simple leaching procedure from Eastman Kodak Co. material of technical grade.⁴ The leached residue, filtered on a Büchner funnel, was washed successively with cold water, alcohol and ether. The final product, which was found to be sulfate free, was air dried for a day and then ground and stored over Anhydron. It melted at 205°, in agreement with Cupery's report,^{2a} and titration with 0.2 *N* sodium hydroxide showed it to be 99.9% pure.

(1) From the M.S. thesis of Mr. B. Selikson, New York University, January, 1945.

(2) (a) Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938); (b) Gordon and Cupery, *ibid.*, **31**, 1237 (1939); (c) Cupery and Gordon, *ibid.*, **34**, 792 (1942).

(3) Audrieth, Sveda, Sisler and Butler, *Chem. Rev.*, **26**, 49 (1940).

(4) The nature of this technical material was such that the more elaborate but necessarily more wasteful purification described by Butler, Smith and Audrieth (*Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938)) was not necessary.

The test for sulfate in solutions either of sulfamic acid or of its salts was made by adding about 5 ml. of saturated barium chloride solution to 1 g. of the sulfamate in 2 ml. of distilled water. If a haze of barium sulfate precipitate did not appear within thirty minutes the material was accepted as "sulfate free." It was otherwise rejected or purified further, although it was estimated, by actual tests with added quantities of soluble sulfate, that as little as a few thousandths of a per cent. of sulfate would give a positive test. The retardation of the precipitation of barium sulfate by sulfamic acid, observed by Divers and Haga,⁵ was not found to occur under the conditions of the test here employed. Premixing of sulfuric acid with sulfamic acid gave precipitates of barium sulfate of the same intensity almost as quickly as did experiments on pure sulfuric acid.

B. Ammonium sulfamate was prepared both by neutralization of sulfamic acid with aqueous ammonia and by recrystallization of technical grade material. The final, recrystallized salt was sulfate-free, melted without decomposition at 131° in agreement with literature values.^{2a,6} and was found to be 99.9% pure on the basis of ammonia content. Ammonia was determined by standard procedure, distilling with excess of potassium hydroxide into boric acid solution and titrating the ammonium borate with 0.2 *N* hydrochloric acid. The amide group of the sulfamates does not interfere in this ammonia determination, as the hydrolysis, producing ammonia and sulfate, is prevented in alkaline solution. Parallel determinations for ammonia content made on pure samples of sulfamic acid, ammonium sulfamate and mixtures of the two, showed no ammonia in the first set of experiments and no effect of sulfamic acid in the latter two. The effect of acidity on

(5) Divers and Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

(6) Berglund, *ibid.*, **34**, 643 (1878).