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o-NITROSOPHENOLS. II. NEW SUBSTITUTED o-NITROSOPHENOLS AND CHARACTERISTIC PROPERTIES OF THEIR INNER COMPLEX METAL SALTS¹

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In the previous part, o-nitrosophenol and its inner complex metal compounds were described (1). By applying the Baudisch reaction (2) to benzene and phenol derivatives, over 50 new mono- and di-substituted o-nitrosophenols could be prepared.

It is not intended to make a detailed survey of the literature of substituted o-nitrosophenols. Besides the previously mentioned nitrosophenol derivatives, such compounds as 4-nitrosoresorcinol, 5-nitrosohydroquinone and 2-nitrosophloroglucinol as well as some of their derivatives, are described in the older literature (3). There are only two observations on these compounds which have a direct relation to the present work. The first concerns the rearrangement of o-nitrosophenols into o-quinoneoximes and vice versa. Due to the much greater stability of the nitroso derivatives of resorcinol it is possible to obtain both isomeric forms in the solid state. Thereby, it has been found that the nitrosophenol form is always green while the quinoneoxime is always yellowish brown (4). This coincides with observations which have been described in the previous part.

The second interesting fact is the observation by Fèvre (1883) (5) that nitrosoresorcinol gives with ferrous sulfate, in aqueous solution, a characteristic green color which can be detected even in a dilution of 1 part in 10 million. The corresponding green ferrous compound of *o*-nitrosophenol has been introduced recently for the colorimetric estimation of divalent iron (6).

Monosubstituted o-nitrosophenols. In the present investigation, the Baudisch reaction was successfully applied to a number of monosubstituted benzene and phenol derivatives, summarized in Table I. Since the new compounds were "trapped" in the form of their reddish violet copper salts, there can be no question as to their having an o-nitrosophenol or o-quinonemonoxime chelate grouping. Consequently, if the starting material is an o- or p-substituted phenol, the configuration of the resulting o-nitrosophenol derivative is definite. It is only in the case of m-substituted phenols that two configurations are possible. The observations which form the basis for the (tentative) formulas assigned to these compounds in this table will be explained later in detail.

It can be seen that the list of monosubstituted *o*-nitrosophenols comprises almost every type of benzene derivative, thus showing the wide applicability of the Baudisch reaction. The compounds were selected with the purpose of investigating as many different types as possible and are not to be regarded as a systematic study of substituted *o*-nitrosophenols.

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	0-NITROSOPHENO	TS	
FARENT COMPOUND	RESULTING 0-MITROSOPHENOL DERIVATIVE	PARENT COMPOUND	RESULTING 0-NITROSOPHENOL DERIVATIVE
l'oluenc	(3)-Methyl-6-nitrosophenol	Guaiacol	
-Cresol	2-Methyl-6-nitrosophenol	Propiophenone	(3)-Propionyl-6-nitrosophenol
n-Cresol	(3)-Methyl-6-nitrosophenol	o-Propionylphenol	2-Propionyl-6-nitrosophenol
p-Cresol	4-Methyl-6-nitrosophenol	$p ext{-} Propionyl phenol$	4-Propionyl-6-nitrosophenol
Ethylbenzene	(3)-Ethyl-6-nitrosophenol	Phenolphthalein	
2-Ethylphenol	2-Ethyl-6-nitrosophenol	Fluorobenzene	(3)-Fluoro-6-nitrosophenol
m-Ethylphenol	(3)-Ethyl-6-nitrosophenol	Chlorobenzene	(3)-Chloro-6-nitrosophenol
v-Ethylphenol	4-Ethyl-6-nitrosophenol	o-Chlorophenol	2-Chloro-6-nitrosophenol
p-Isopropylphenol	4-Isopropyl-6-nitrosophenol	m-Chlorophenol	(3)-Chloro-6-nitrosophenol
<i>p-tert.</i> -Butylphenol	4-tertButyl-6-nitrosophenol	p-Chlorophenol	4-Chloro-6-nitrosophenol
p-tertAmylphenol	4-tertAmyl-6-nitrosophenol	Bromobenzene	(3)-Bromo-6-nitrosophenol
Phenylacetylene		o-Bromophenol	2-Bromo-6-nitrosophenol
2-Phenylphenol	2-Phenyl-6-nitrosophenol	p-Bromophenol	4-Bromo-6-nitrosophenol
o-Benzylphenol	2-Benzyl-6-nitrosophenol	o-Iodophenol	2-Iodo-6-nitrosophenol
p-Benzylphenol	4-Benzyl-6-nitrosophenol	Nitrosobenzene	
Benzyl alcohol		Nitrobenzene	
Salicylic alcohol	2-Hydroxy-3-nitrosobenzyl alcohol	Benzenesulfonic acid	
Salicylic acid	2-Hydroxy-3-nitrosobenzoic acid	Benzenesulfonamide	
p-Hydroxybenzoic acid	4-Hydroxy-3-nitrosobenzoic acid	Tyrosine	3-Nitroso-4-hydroxyphenylalanine
n-Propyl- p -hydroxybenzoate			

TABLE I

8

GEORG CRONHEIM

There are two groups of benzene derivatives in which the Baudisch reaction usually fails; namely, aromatic aldehydes and primary amines. In the case of amines, the reaction will lead to diazo compounds, while the aldehyde group reacts with the nitrosyl radical or with hydroxylamine directly to form hydroxamic acids or oximes respectively (Angeli reaction). Some exceptions will be mentioned later.

The properties of all substituted *o*-nitrosophenols are very similar to those of *o*-nitrosophenol. The free compounds can be shaken out with organic solvents from acidified aqueous solutions of their copper salts. Petroleum ether will dissolve readily all investigated *o*-nitrosophenols with the exception of those obtained from tyrosine, benzenesulfonamide, and sulfanilamide where ether or ethyl acetate is preferable.

The inner complex metal compounds which are so characteristic for the *o*-nitrosophenol (*o*-quinonemonoxime) grouping may be formed and investigated as previously described (1). Their outstanding properties (color and solubility) are summarized in Tables II and III.

It is quite apparent that all these salts, although very similar, are not absolutely uniform. In most cases the variations are not so much due to the substituent itself, but rather to its position relative to the *o*-nitrosophenol grouping. In order to simplify the following descriptions, the substituted *o*-nitrosophenols will be designated by the phenol from which they were obtained.

Outstanding among the variations is the color of the cobalt compounds in solution. All those obtained from ortho-substituted nitrosophenols are grayish violet, while all those obtained from meta- and para-substituted nitrosophenols are reddish brown. This rule has been verified in all cases where the substituent is an alkyl, phenyl, halogen, or carboxyl group.

A similar rule concerns the solubility of the cupric, mercuric, ferrous, and nickel salts. The complexes of type I are, under the outlined experimental conditions, without exception soluble in water. As to the complexes of type II, only those derived from ortho-substituted phenols are soluble in water, while those of meta- and para-substituted nitrosophenols are completely insoluble in both water and petroleum ether. In many cases, the metallic ions (especially copper and mercury) can thus be precipitated quantitatively even from highly dilute solutions.

The only seeming exceptions to this rule are alkyl nitrosophenols where the alkyl group contains three or more carbon atoms. These compounds will be described in greater detail in a following paper.

In the case of ferrous and nickel salts, the precipitation is not quantitative as indicated by the fact that the aqueous phase still is characteristically colored. Apparently the formation of the nitrosophenol complexes II does not proceed as easily as with copper and mercury, and the color of the water is due to some ferrous or nickel compounds of type I.

The solubility of the metal compounds of type II in organic solvents other than petroleum ether is not affected by substituents and is, therefore, the same as that of simple nitrosophenol salts.

TABLE II

Solubility in Water and Ether of the Two Types of Inner Complex Compounds of Monosubstituted o-Nitrosophenols with Copper, Mercury, Divalent Iron, and Nickel (Metals of Group 1a)

						coz	PLE?	с сом	POUN	id wi	TH					
		Cu	l++			Hg	++			Fe	;++	1		Ni	++	
						Colo	rofo	omp	lex co	ompo	und					
	1	Red-v	iolet			Re	d			Gree	en			Re	1	
0-NITROSOPHENOL OBTAINED FROM:					T	ype c	of cor	nplez	con	pour	nd					
	I		I	I	I		I	I	I		I	I	I		I	I
					1		S	، olubi	lity i	n				+		
			.	. 1	5	.					-	ы	Ь			
	Wate	Ethe	Wate	Ethe	Wate	Ethe	Watc	Ethe	Wate	Ether	Wate	Ethe	Wate	Ethe	Wate	Ether
a-Cresol	+		-+-	+	+	_	-+-	+	+	_	-		+	_	+	
m-Cresol			_	+		_	'	+	<u>+</u>			+			4	-+-
n-Cresol		_		+	+			+	<u>+</u>	_	_	+	+	_	_	+
o-Ethylphenol	-	_	+	+	4		-+-	4	_	_	+	'	+		+	'
m-Fthylphenol				4		_	'	4		_		+	+		1	+
<i>n</i> -Ethylphenol		_	_	4	4	_		+				+		_		+
n Isopropylphenol			_	4		_	_	4		_	_		-	_		+
<i>m_tert</i> _Butyphenol		_	_	+	4	_	_				_					4
m tert Amylphenol		_				_	_	4			_		<u>+</u>			
Phonyla ostylano	- T-							_	-		_					1
a Phonylphonal											Ì					
a Bangwinhanal																
n Benzylphenol					T											
P-Denzylphenol				_1	-											
Selienlie elechel	+	_			-					-					Ì	
Denovie and	+-	-		+				Ţ		_			-			
		_				-		+	+	-				_	1	
o-Hydroxybenzoic acid	+	-			+	-		+	+	-			+	-		
<i>p</i> -Hydroxybenzoic acid	+			+	+			+	+				+		ĺ	
<i>n</i> -Propyl <i>p</i> -nydroxybenzoate	+				+				+							
Gualacol	+				-+				+			. 1				,
Propiopnenone		-	_	+	+	-	_			-	_	+		_	_	+
o-PropionyIphenol	-+-		+	+	+		+	+	+		-+-	+	+		+	+
<i>p</i> -Propionylphenol	+		-	+	+		-	+	+	-	-	+	-+-		-	+
Phenolphthalein	+				+				+				-+-			
Fluorobenzene	+				++				+				+			
Chlorobenzene	+	-		+									-+-		+	+
o-Chlorophenol	+		+	+	+	-	+	+	+	_	+		-+-	-	+	+
<i>m</i> -Chlorophenol	+	-		+	+	-		+	+	_	+	+	+	- 1	+	+
<i>p</i> -Chlorophenol	+			+	+	-		+	+	-	-	+	+	-	-	+
Bromobenzene	+												+			
o-Bromophenol	+	-	+	+	+	-	+	+	+	-	+	-	+		+	+
<i>p</i> -Bromophenol	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+
o-Iodophenol	+	-	+	+	+		+	+	+		+	-	+	-	+	+
Nitrosobenzene	+				+				+				+			
Nitrobenzene	+				+				+				+			
Benzenesulfonic acid	+			+	+			+	+				+			
Benzenesulfonamide	+	ĺ		+	+			-	+				+			
Tyrosine	+				+				+		1 '	1	+		i	

The "pyridine effect" (Table IV) likewise is in all cases the same as with simple *o*-nitrosophenol with one exception. All mercuric compounds of para-substituted nitrosophenols remain insoluble in petroleum ether even after addition of pyridine and in the presence of an excess of the free nitrosophenol. They can thus be differentiated from the corresponding cupric compounds.

All of the ferrous compounds show a positive pyridine effect. However, usually it is necessary to add the pyridine to the aqueous ferrous salt solution before shaking with the free nitrosophenol.

Another rule concerns the solubility of various lead complexes. The affinity of this metal towards most *o*-nitrosophenols is not very strong, the resulting solutions being only light pink in color. However, lead shows a characteristic pyridine effect, namely, the formation of a deep red precipitate with all parasubstituted nitrosophenols. This effect was never observed with ortho- or meta-substituted nitrosophenols.

This reaction is very helpful in distinguishing between meta- and parasubstituted nitrosophenols—a differentiation which cannot be made either by the color of the cobalt compounds or by the solubility of copper or mercury compounds. There is only one condition in which this reaction cannot be applied. A few substituted nitrosophenols (o- and p-bromonitrosophenol) have been found to possess very strong affinities for lead and to form directly the corresponding lead compounds, which are insoluble in water and petroleum ether. The precipitation seems to be quantitative and is not affected by the addition of pyridine.

Another interesting rule concerns the nitrosophenol complexes of trivalent iron, where not only the nature of the substituent, but also its position, is of importance. The affinity of ordinary *o*-nitrosophenol for ferric ions is so weak that the formation of the ferric complex which is soluble in petroleum ether can hardly be detected. The same is true for a number of substituted nitrosophenols (nitroso derivatives of *o*-chlorophenol, benzoic acid, salicylic acid, etc.) while others show very distinctly the formation of a ferric complex, soluble with brown color in petroleum ether. In all cases, where such a comparison could be made, it has been found that the meta- and para-substituted nitrosophenols result in much darker solutions with ferric salts than the ortho-substituted compounds. Whether this is due to differences in the color of the ferric complexes or differences in the affinity of the nitrosophenols to ferric ions, has not been investigated.

Of other metals with a selective affinity for substituted nitrosophenols only silver will be mentioned. It forms red precipitates with the nitrosophenols obtained from p-chloro- and p-bromo-phenol as well as from phenylacetylene.

From the foregoing it is evident that the nitroso derivatives of meta- and para-substituted phenols resemble each other rather closely in their metal compounds, but are distinctly different from ortho-substituted nitrosophenols. If one looks at the four possible configurations it appears probable that there should exist two groups of compounds, one in which the substituent R is in the immediate vicinity and another in which it is separated from the chelate

IRON (METALS OF GROUP IN), AND WITH ZINC,	LEAD, AND SILVER (N	LETALS OF G	ROUP 2)	
			COMPLEX COMPOUND WIT	Н		
	Co++	++Pd	Fe+++	Zn++	Pb++	Ag ⁺
0-NITROSOPHENUL OBTAINED FRUM:		c	olor and solubility of metal c	omplex in		
<u>. </u>		Petroleum ether			Water	
o-Cresol	gray	green	very light brown			
m-Cresol.	red brown	green	dark brown			
p-Cresol	red brown	green and precip.	dark brown		pink	
o-Ethylphenol	gray	green	very light brown			
m-Ethylphenol	red brown	green	dark brown			
<i>p</i> -Ethylphenol	red brown	green and precip.	dark brown		pink	
<i>p</i> -Isopropylphenol	red brown		brown			
<i>p-tert.</i> -Butylphenol	red brown		brown	pink?		
<i>p-tert.</i> -Amylphenol	red brown		brown			
Phenylacetylene	gray	green	brown			brown precip.
o-Phenylphenol	gray	green	brown	pink?	pink	
o-Benzylphenol	gray	green				
p-Benzylphenol	red brown	green				
Benzyl alcohol.	brown	green		pink	pink	
Salicylic alcohol	brown	green	pink	pink?	pink	
Benzoic acid	gray	green				
o-Hydroxybenzoic acid	gray	green				
<i>p</i> -Hydroxybenzoic acid	red brown	green		pink	pink	pink?
n-Propyl-p-hydroxybenzoate.	red brown	green				
Guaiacol	red brown and pre-	green	brown			
	cip.					
Propiophenone	red brown and pre-	green and precip.	brown			
	cip.					
o-Propionylphenol	gray and precip.	green and precip.	brown and precip.	pink?	pink	-

COLOR AND SOLUBILITY OF THE INNER COMPLEX COMPOUNDS OF MONOSUBSTITUTED 0-NITROSOPHENOLS WITH COBALT, PALLADIUM, TRIVALENT TABLE III

12

GEORG CRONHEIM

<i>p</i> -Propionylphenol	red brown and pre-	green and precip.	dark brown and pre-	pink?	pink	
	cip.		cip.			
Phenolphthalein	red brown	green and precip.	dark brown			
Fluorobenzene	red brown					
Chlorobenzene	red brown					red precip?
o-Chlorophenol	gray	green	very light brown	pink?	pink?	pink?
m-Chlorophenol	red brown	.green	dark brown	pink?	pink?	red precip.?
<i>p</i> -Chlorophenol	red brown	green and precip.	dark brown	pink	pink	
Bromobenzene	gray					
o-Bromophenol.	gray	green and precip.	light brown	pink	red precip.	pink?
p-Bromophenol.	red brown	green and precip.	dark brown	pink	red precip.	red precip.
o-Iodophenol	gray	green		pink	pink	pink?
Nitrosobenzene.	gray	-		- 4		
Nitrobenzene	brown					
Benzenesulfonic acid	gray	green and precip.	very light brown	pink?	pink	pink?
Benzenesulfonamide	red brown	green				
Tyrosine	red brown					
"?" indicates that under the	e conditions used the	formation of the m	etal complex is questi	onable.		

0-NITROSOPHENOLS. II

13

grouping. Thus the similarity of the metal compounds of meta- and parasubstituted nitrosophenols in contrast to ortho-substituted ones decides in



TABLE IV

"PYRIDINE EFFECT" OF MONOSUBSTITUTED O-NITROSOPHENOLS Upon addition of Pyridine the metal complex

becomes soluble in petroleum ether +

		F F F F F F F F F F F F F F F F F F F	
forms a	red precipi	itate	P

ANTERSORDENCE ORTAINED FROM			COME	LEX COM	POUNDS P	ORMED W	ITH:		
	Cu++	Hg++	Fe++	Ni++	Zn++	Pb++	Ag+	Cd++	
o-Cresol	+	+	+	+	+	_			
<i>m</i> -Cresol	+	+	+	+	+	-			
<i>p</i> -Cresol	+	-	+	+	+	Р			
o-Ethylphenol	+	+	+	+	+	-			
<i>m</i> -Ethylphenol	+	+	+	+	+				
<i>p</i> -Ethylphenol	+		+	+	+	Р			
<i>p-tert</i> Butylphenol					+	Р			
Phenylacetylene	+	-	+	+	+	Р			+
o-Phenylphenol	+	+	+	+	+		?	+-	+
Salicylic alcohol	+	+	+	+					
Salicylic acid	+	+	+	+					?
Guaiacol	+	+	+	+					
Propiophenone	+		+	?			*		
o-Propionylphenol	+	+	+	+					
p-Propionylphenol	+	-	+	?		Р			
Fluorobenzene	+	+	+	+					
o-Chlorophenol	+	—	+	+	+				
m-Chlorophenol	+	-	+	+		-	+		
p-Chlorophenol	+	-	+	+	+	Р		+	
o-Bromophenol	+	—	+	+	+	_	-	+	+
p-Bromophenol	+	-	+-	+	+	_	-	+	+
Nitrobenzene	+		+	+					
Benzenesulfonamide	+	+	+	+				+	

"?" indicates that under the conditions used the formation of the metal complex is questionable.

favor of formula III for meta-substituted nitrosophenols. Accordingly, their general formula should be 3-R-6-nitrosophenol. Further evidence as to the correctness of this formula, will be given in a subsequent paper, together with the formulas of alkyl substituted nitrosophenols which were obtained directly from the benzene instead of the phenol derivatives. Disubstituted o-nitrosophenols. Heretofore, only nitrosophenols with one substituent have been mentioned. The Baudisch reaction can, however, be applied successfully also to benzene and phenol derivatives with more than one substituent. Examples are given in the following list of compounds all of which formed the corresponding o-nitrosophenols (Table V).

The number of these compounds is not very great but sufficient to prove two points (Tables VI-VIII):

1. Even if the benzene ring contains two substituents, either of the same or of different kinds, it is possible to introduce by means of the Baudisch reaction, a hydroxyl and a nitroso group.

PARENT COMPOUND	RESULTING 0-NITROSOPHENOL DERIVATIVE
o-Xylene	(3,4)-Dimethyl-6-nitrosophenol
3,4-Dimethylphenol	3,4-Dimethyl-6-nitrosophenol
3-Methyl-4-chlorophenol	3-Methyl-4-chloro-6-nitrosophenol
<i>m</i> -Xylene	(2,4)-Dimethyl-6-nitrosophenol
2,4-Dimethylphenol	2,4-Dimethyl-6-nitrosophenol
3,5-Dimethylphenol	3,5-Dimethyl-6-nitrosophenol
<i>p</i> -Xylene	2,5-Dimethyl-6-nitrosophenol
2,5-Dimethylphenol	2,5-Dimethyl-6-nitrosophenol
5-Methyl-2-isopropylphenol	5-Methyl-2-isopropyl-6-nitrosophenol
2,4-Diamylphenol	2,4-Diamyl-6-nitrosophenol
2,3-tertDibutyl-4-methylphenol	(2,3)-tertDibutyl-4-methyl-6-nitrosophenol
o-Diphenylbenzene	(3,4)-Diphenyl-6-nitrosophenol
o-Fluorotoluene	
<i>m</i> -Fluorotoluene	
p-Fluorotoluene	
<i>m</i> -Chlorotoluene	
<i>p</i> -Chlorotoluene	
o-Dichlorobenzene	
p-Chlorobromobenzene	
o-Nitroanisole	
o-Nitrobenzaldehyd	
Sulfanilamide	

TABLE V DISUBSTITUTED 0-NITROSOPHENOLS

2. The presence of more than one substituent does not alter the typical properties of the *o*-nitrosophenol chelate grouping.

Concerning the various dimethylnitrosophenols (nitrosoxylenoles) a more detailed description will be given in a subsequent paper.

In the list of disubstituted benzene derivatives are two compounds belonging to those two groups which usually do not form an o-nitrosophenol in the Baudisch reaction. These two compounds are o-nitrobenzaldehyde and sulfanilamide, representing aldehydes and primary aromatic amines respectively. The reason for the atypical behavior is obvious in the case of o-nitrobenzaldehyde. It is known that this compound exists in two isomeric forms, one of which has lost completely its aldehyde character. It is probably the latter which reacts in the Baudisch reaction to form a substituted *o*-nitrosophenol.



TABLE VI

SOLUBILITY IN WATER AND ETHER OF THE TWO TYPES OF INNER COMPLEX COMPOUNDS OF DISUBSTITUTED O-NITROSOPHENOLS WITH COPPER, MERCURY, DIVALENT IRON, AND NICKEL (METALS OF GROUP 1a)

						COL	APLES	к сом	(POU)	vd w	ITH					
		Cu	ı++			H	s++			Fe	++			Ni	.++	<u> </u>
					·	Colo	r of	comp	lex c	ompo	ound					
		Red-	viole	t		Re	ed			Gr	een			R	ed	
0-NITROSOPHENOL OBTAINED FROM:					<u> </u>	Тур	e of o	omp	lex co	ompo	ound					
]	[I	I	I		I	I	I		I	I	1	[I	I
					1		s	olubi	lity i	n		1				
	5	H	*	н	1	2	1		ы		۲.	5	18	н	H	н
	Wate	Ethe	Wate	Ethe	Wate	Ethe	Wate	Ethe	Wat	Ethe	Wat	Ethe	Wat	Ethe	Wate	Ethe
3.4-Dimethylphenol	+							+	+				+			+
2,4-Dimethylphenol	+				+				+				+			
3,5-Dimethylphenol	+			+	+		_	+	+			+	+		_	+
2,5-Dimethylphenol	+				+				+				+			
2,4-Diamylphenol	+				+				+				+			
Thymol	+	-	-	+	+	-	-	+	+	-		+	+		-	+
o-Diphenylbenzene	+				+				+				+			
o-Fluorotoluene	+				+				+				+			
m-Fluorotoluene	+				+				+				+			
p-Fluorotoluene	+				+				+				+			
<i>m</i> -Chlorotoluene	+				+				+				+			
<i>p</i> -Chlorotoluene	+				+				+				+			
3-Methyl-4-chlorophenol	+		-	+	+		-	+	+			+	+		-	+
o-Dichlorobenzene	+	-	-	+	+	-	-	+	+		-	+	+	-		+
<i>p</i> -Chlorobromobenzene	+				+				+				+			
o-Nitroanisole	+	-			+				+	-			+	-		
o-Nitrobenzaldehyde	+				+				+					1		
Sulfanilamide	+			+	+		1		+				+			

Preparation of p-substituted o-nitrosophenols. The fact that copper salts of type II of all p-substituted nitrosophenols are insoluble in water can be utilized

for the preparation of these compounds. The principle consists in the nitrosation of a p-substituted phenol in the presence of the proper amount of a cupric salt and the maintenance of the correct pH. The formed nitrosophenol immediately combines with the cupric ion and is thus precipitated as an almost pure copper salt.

TABLE VII

COLOR AND SOLUBILITY OF THE INNER COMPLEX COMPOUNDS OF DISUBSTITUTED O-NITRO-
sophenols with Cobalt, Palladium, Trivalent Iron (Metals of Group 1b), and
with Zinc, Lead, and Silver (Metals of Group 2)

			COMPLEX COMPOU	ND WITH		
A NYTROCODUCION OF ANTED PROV	Cu++	Pd++	Fe ⁺⁺⁺	Zn++	Pb++	Ag+
O-AITROSOPHENOL OBTAINED FROM.		Color a	and solubility of 1	netal com	plex in	
	Pet	roleum Et	her		Water	
3,4-Dimethylphenol	red brown	green	light brown	pink?		
3,5-Dimethylphenol	gray brown	green	brown	pink	pink?	pink?
2,4-Diamylphenol Thymol	brown gray gray	green		pink	pink?	
o-Fluorotoluene m-Fluorotoluene	red brown brown		brown	pink?		
<i>m</i> -Chlorotoluene <i>p</i> -Chlorotoluene	gray brown	green	brown light brown?	pink pink	pink pink	
3-Methyl-4-chlorophenol	brown	green	light brown?	pink	pink	
o-Dichlorobenzene p-Chlorobromobenzene o-Nitroanisole o-Nitrobenzaldehyde	red brown brown gray gray	green green green	brown light brown light brown	pink pink pink	red precip. pink pink	pink pink?
Sulfanilamide	red brown		light brown			

"?" indicates that under the conditions used the formation of the metal complex is questionable.

Twelve and nine-tenths grams (0.1 mole) of *p*-chlorophenol is dissolved in 30 ml. of glacial acetic acid. This solution is diluted with 50 ml. of water and sufficient sodium acetate is added to bring the *p*H to 4.2. To this mixture is added a solution of 17.3 g. (0.25 mole) of sodium nitrite and 12.5 g. (0.05 mole) of crystalline cupric sulfate in 500 ml. of water. The mixture turns deep green immediately and then darkens quickly. After several days standing at room temperature, the precipitated copper salt of 4-chloro-6-nitrosophenol can be filtered off. About 50% of the theoretical amount will be formed during the first three days. The total yield reaches about 80-85% after two weeks. The dried crude precipitate is about 90% pure and can be recrystallized from an alcohol-chloroform (2:3) mixture.

Anal. Calc'd for C12H6Cl2CuN2O4: Cl, 18.8; Cu, 16.9.

Found: Cl, 19.0; Cu, 16.7.

The free chloronitrosophenol in crystalline form can be obtained in the following manner:

The copper salt is suspended in normal sulfuric acid and shaken repeatedly with petroleum ether. These extracts are washed twice with ice-water and then shaken with a small amount of normal sodium hydroxide solution. Upon careful neutralization of the ice-cold solution of the sodium salt with normal sulfuric acid the free chloro-o-quinonemonoxime is precipitated in the form of small yellowish brown needles. They are filtered off, washed with ice-water and dried in the desiccator; m.p. 40-41° uncorr.

The same procedure has been applied with equally good results to form the copper salts and the free o-nitrosophenols, respectively from p-cresol and p-bromophenol.

TABLE VIII

"Pyridine Effect" of Disubstituted o-Nitrosophenols

Upon addition of pyridine the metal complex

becomes soluble in petroleum ether + remains insoluble in petroleum ether forms a red precipitate P

0-NITROSOPHENOL OBTAINED FROM:			COM	PLEX COM	POUNDS E	ORMED W	ITH		
	Cu++	Hg++	Fe++	Ni++	Zn++	Pb++	Ag+	Cd++	Ti+++
3,4-Dimethylphenol 2,4-Dimethylphenol 3,5-Dimethylphenol Thymol o-Diphenylbenzene	+++++++++++++++++++++++++++++++++++++++	+++++++++++++++++++++++++++++++++++++++	+++++++++++++++++++++++++++++++++++++++	+++++++++++++++++++++++++++++++++++++++	? P +	– P P +	?	?	ç
m-Fluorotoluene	+ + + + + + +	- + + + + + + + + + + + + + + + + + + +	+++++++++++++++++++++++++++++++++++++++	+++++++++++++++++++++++++++++++++++++++	+++++++++++++++++++++++++++++++++++++++	P P 	5		÷

"?" indicates that under the conditions used the formation of the metal complex is questionable.

Anal. Calc'd for $C_{14}H_{12}CuN_2O_4$: Cu, 18.95. Found: Cu, 18.5. The free o-nitrosophenol $C_7H_7NO_2$, had the m.p. 56-58° uncorr. Anal. Calc'd for $C_{12}H_6Br_2CuN_2O_4$: Br, 34.4. Found: Br, 34.9. The free o-nitrosophenol, $C_6H_4BrNO_2$, had the m.p. 51-53° uncorr.

SUMMARY

By using the Baudisch reaction 33 new mono- and 19 new di-substituted o-nitrosophenols have been prepared and some of their inner complex metal salts have been investigated. The color and the solubility of these metal complexes show very definite relationships to the configuration of the substituted o-nitrosophenols.

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