drawing nature of the substituent group. The nitrogen adjacent to the electron-withdrawing group will be the site of attack. The final product will be the same by either mechanism. The latter mechanism is similar to that postulated by Ulrich[12] to account for the formation of N,N′-di-*n*-butyl-N′-chloroformylchloroformamidine by phosgenation of N,N′-di-*n*-butylurea in the presence of triethylamine. Further, the addition of phosgene to carbodiimides at room temperature is well established.[11]

A related series involves the reactions of N,N′-dicyclohexylurea with N,N′-dicyclohexyl- and N,N′-diphenylchloroformamidine hydrochloride at 115° in the absence of phosgene. The expected guanidine was isolated from the former reaction. In the latter, there was no indication of the formation of trisubstituted guanidines. This establishes that the nature of the chloroformamidine and not the urea is the overriding factor in determining the extent of guanidine formations.

In summary, a novel method for the synthesis of N,N′,N″-substituted guanidines is presented. This type of compound results from the phosgenation of ureas containing electron-donating groups. In contrast, the complete absence of guanidine formation is observed in cases where all the substituent groups on the ureas are electron withdrawing or one of the substituents is strongly electron withdrawing. Reaction mechanisms are postulated to explain these observations.

Registry No.—IV, 498-63-5; V, 13134-13-9; N,N′,-N″-tricyclohexylguanidine hydrochloride, 13134-14 0; N,N′-dicyclohexyl-N″-isopropylguanidine hydrochloride, 13134-15-1; N-cyclohexyl-N′,N″-diisopropylguanidine hydrochloride, 13134-16-2; N-cyclohexyl-N′,N″-diethylguanidine hydrochloride, 13134-17-3; N,N′-dicyclohexyl-N″-phenylguanidine, 13134-18-4; N,N′-diisopropyl-N″-diphenylguanidine, 13134-19-5; diphenylcarbodiimide trimer, 13136-42-0.

Studies on the Baudisch Reaction. I. The Synthesis of *o*-Nitrosophenols

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The reaction mechanism of the Baudisch reaction, which is the synthetic reaction of *o*-nitrosophenols from benzene or substituted benzenes, hydroxylamine hydrochloride, and hydrogen peroxide in the presence of copper(II) ion, has been reinvestigated. The phenolic hydroxyl group plays an important role in this reaction and the marked steric influence of a methyl group at the position *meta* to the phenolic hydroxyl group was observed on nitrosation at the position *ortho* to both the methyl and the hydroxyl groups. These results support the hypothesis that a bulky copper–hydroxylamine comlpex is involved in this specific *o*-nitroso hydroxylation. It was found also that nitrous acid, which had been proposed previously as the true nitrosation agent in this reaction, was unable to give the product ratio of *o*- to *p*-nitrosophenol which is observed in the Baudisch reaction.

In the presence of copper(II) ion, a solution containing aqueous hydroxylamine hydrochloride and hydrogen peroxide reacts with benzene or phenol to give *o*-nitrosophenol. This reaction was discovered by Baudisch[2] about 25 years ago. Cronheim[3] has further developed the Baudisch reaction to prepare a variety of *o*-nitrosophenols from the corresponding substituted benzenes.

Concerning the mechanism of this reaction, Baudisch[4] and Cronheim[3] postulated that the copper(I) nitrosyl ion, $CuNO^+$, attacks the aromatic ring leading to nitrosation and that hydroxylation adjacent to the position attacked follows this nitrosation. They made the tentative hypothesis that the copper(I) nitrosyl ion was formed from Cu(I) and nitrosyl radicals which had been generated *via* prior oxidation–reduction reactions among the various reagents. Moreover, they suggested that by forming a complex with the resultant *o*-nitrosophenol, the Cu(II) ion plays a role in preventing further oxidation to *o*-nitrophenol and rearrangement to *p*-nitrosophenol. More recently, Konecny[5] has proposed a mechanism in which nitrous acid produced by the reaction of hydroxylamine and hydrogen peroxide is postulated to act as a nitrosation agent for the phenol which had been produced by the hydroxylation of benzene. This hypothesis was supported by the fact that hydroxyl radicals could be produced from hydrogen peroxide through the catalytic action of Cu(II) ion.[6] However, no systematic investigation of this reaction has ever been reported.

Since this unusual exclusive *o*-nitroso hydroxylation of aromatics was of considerable interest and since the mechanism by which the reaction occurs was in doubt, we reinvestigated the reaction and have come to the conclusion that this reaction does not follow the mechanisms proposed by former investigators.

Results and Discussion

Rate of Formation of *o*-Nitrosophenols.—As *o*-nitrosophenols are extremely volatile and readily oxidized in air, it is difficult in general to isolate them and determine their concentrations. Fortunately, these *o*-nitrosophenols form stable copper(II) complexes which have an intense red color in aqueous solution. The spectra of the copper complexes in water showed characteristic absorption maxima at *ca.* 420 and *ca.* 530 mμ in the visible region and at about 340 mμ in the ultraviolet region. The absorption band at *ca.* 340 mμ was the most intense and could be used alone for the determination of the concentration of *o*-nitrosophenols. We followed the rates of formation of

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[1] (a) Kyoto University; (b) Kyoto Women's University.

[2] O. Baudisch, *Naturwissenschaften*, **27**, 768 (1939); O. Baudisch and S. H. Smith, *ibid.*, **27**, 769 (1939).

[3] G. Cronheim, *J. Org. Chem.*, **12**, 1 (1947).

[4] O. Baudisch, *Science*, **92**, 336 (1940); *Arch. Biochem.*, **5**, 301 (1944).

[5] J. O. Konecny, *J. Am. Chem. Soc.*, **77**, 5748 (1955).

[6] J. O. Konecny, *ibid.*, **76**, 4993 (1954).

o-nitrosophenols for some of aromatics under the conditions of the Baudisch reaction. The aromatics investigated were benzene, toluene, chlorobenzene, anisole, phenetole, methyl *p*-tolyl ether, phenol, 2,6-, 2,3-, 2,5-, and 3,5-xylenol, *o*-, *m*-, and *p*-cresol, and *m*- and *p*-chlorophenol. The results obtained are shown in Figure 1. All the reactions were conducted under a nitrogen atmosphere.

o-Nitroso hydroxylation of benzene or substituted benzenes having no hydroxyl group proceeded much more slowly than that of phenols. Though Cronheim[3] ascribed this high reactivity of phenol to its high solubility in water, this viewpoint is not acceptable, because the same relative reactivity was observed in alcohols which completely dissolved all of the aromatic hydrocarbons and phenols investigated (see Figure 2). Since benzene, anisole, phenetole, and methyl *p*-tolyl ether had no reactivities in methanol at all, it is possible that the hydrogen atom of the phenolic hydroxyl group might be playing some important role in the reaction and that the Baudisch reaction of benzene might be proceeding *via* phenol formation. On the other hand, the difference between the reaction rate of 2,3-xylenol and that of 2,5-xylenol can be interpreted as owing to a steric effect of the methyl group, because the position *ortho* to the hydroxyl group in 2,5-xylenol may be under the influence of the adjacent methyl group, but that of 2,3-xylenol is not. Since both of positions *ortho* to the hydroxyl group in 3,5-xylenol are expected to be under the steric influence of the methyl groups, it is not surprising on steric grounds that this compound was not as reactive as *m*-cresol which has one position *ortho* to the hydroxyl group free from the influence of the methyl group. This steric effect of methyl groups upon the substitution reaction was shown very distinctly in the reaction of *m*-cresol. Whereas both 2-nitroso-*m*-cresol and 6-nitroso-*m*-cresol might be expected as the reaction products, the nitrosation took place almost exclusively at the 6 position which was free from the steric repulsion of the methyl group (Figure 3).

At present, there is no conclusive evidence for the formation of a bulky copper complex at the phenoxy group, but the observed role of the hydrogen atom in the hydroxyl group and the strong steric effect of a methyl group occupying the position *meta* to the hydroxyl group suggest that the reaction may proceed through the intermediate formation of a complex.

The Baudisch reaction in air proceeded at a slightly lower reaction rate than that under nitrogen. The reaction of benzene, phenol, and *p*-cresol in air is compared with that under nitrogen in Figure 4. There is a small but distinct difference between them.

Specific Character of Catalysts.—In the Baudisch reaction, sodium pentacyanoammine ferrate(II) as well as copper(II) nitrate is an effective catalyst.[7a] To determine whether the activity of the pentacyanoammine ferrate(II) ion is connected with the presence of the iron(II) ion, we examined the catalytic activity of iron(II) sulfate.[7b] We also employed copper(II) hydroxide as a catalyst to see whether the nitrate anion associated with the copper(II) ion had some influence on the reaction or not. One can clearly see in Figure 5 that the simple iron(II) ion had only poor catalytic activity whereas the complex iron(II) in pentacyanoammine ferrate(II) had strong catalytic power as well as the copper(II) ion and further that the nitrate ion was not involved in the nitrosation process.

Nitrosation of Phenol.—Although it was confirmed that phenols reacted exceedingly faster than aromatic hydrocarbons to give *o*-nitrosophenols, there remains a doubt why the amounts of the *o*-nitrosophenols found in the Baudisch reaction were much greater than those of the *para* isomer, if the reaction proceeds through an ionic mechanism as postulated by Konecny. In order to get more precise information about the relative production of the *o*- and *p*-nitrosophenols, the following reactions were conducted and the relative product ratios of *o*- to *p*-nitrosophenols were measured: (i) nitrosation of phenol with nitrous acid in the presence or in the absence of the copper(II) ion and (ii) nitrosation of phenol under the conditions of the Baudisch reaction. The *ortho* and *para* isomers were determined spectroscopically after being separated with thin layer chromatography. The nitrosation of phenol with nitrous acid gave about 30 times as much *p*-nitrosophenol as *o*-nitrosophenol. The presence of copper(II) in reaction mixture did not greatly affect the predominant formation of *p*-nitrosophenol, although the *ortho* isomer which was stabilized as the copper(II) salt was found in slightly higher concentration than in the absence of the copper(II) ion. In the Baudisch reactions, in contrast, the amount of the *ortho* isomer produced was about 10–20 times that of the *para* isomer (see Table I). This unambiguous difference in the relative product ratios of the isomers offered decisive evidence that the reaction mechanism in which the cationic nitroso ion was assumed to be the reagent involved in the *ortho* nitrosation of phenol is not acceptable for the Baudisch reaction. It was found also that, contrary to Konecny's suggestion, the nitrosation of phenol, conducted with aqueous hydroxylamine and hydrogen peroxide without any catalysts, proceeded too slowly to give any appreciable amounts of the nitrosophenols. Finally, the experimental findings in our investigation have given decisive information to prove the incorrectness of Konecny's proposal that the nitrous acid which would be generated from hydroxylamine and hydrogen peroxide in the reaction mixture is the *ortho* nitrosation agent for phenol in the Baudisch reaction. The results shown in Table II also indicate

TABLE I

PRODUCT RATIOS OF *o*- TO *p*-NITROSOPHENOL OBTAINED FROM PHENOL UNDER VARIOUS REACTION CONDITIONS[a]

	Nitrosophenols, moles $\times 10^{-4}$			*ortho*/
Reagents	Total	*o*-	*p*-	*para*
$NaNO_2$–buffer[b]	3.85	0.1	3.75	1:37
$NaNO_2$–Cu^{2+}–buffer[b]	4.05	0.4	3.65	1:9
$NH_2OH \cdot HCl$–H_2O_2–Cu^{2+}–buffer[b]	6.55	6.3	0.25	25:1
$NH_2OH \cdot HCl$–H_2O_2–Fe complex[c]	3.24	2.6	0.64	4:1
$NH_2OH \cdot HCl$–H_2O_2–Cu^{2+} [d]	0.56	0.5	0.06	9:1

[a] All reactions were conducted for 30 min at 30°. [b] A Walpole buffer (pH 2.5). [c] Sodium pentacyanoammine ferrate(II). [d] Conducted in methanol.

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[7] (a) O. Baudisch, *J. Am. Chem. Soc.*, **63**, 622 (1941); (b) O. Baudisch originally reported qualitatively on the inactivity of the simple iron(II) ion.

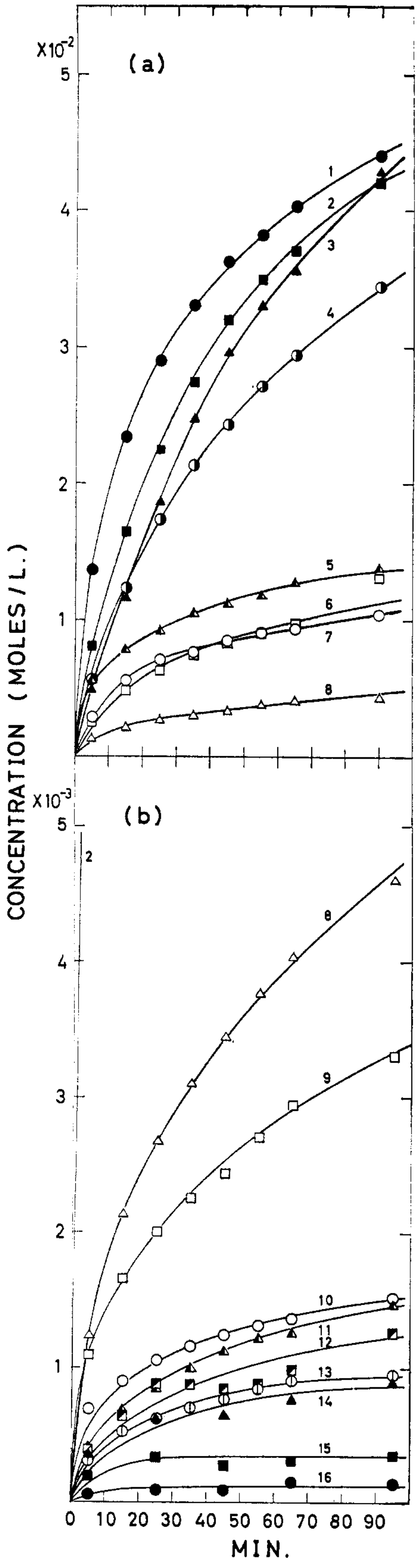

Figure 1.—Rate of formation of *o*-nitrosophenols under Baudisch's conditions at 30° under a nitrogen atmosphere: 1, *m*-cresol; 2, phenol; 3, *m*-chlorophenol; 4, *p*-chlorophenol; 5, *p*-cresol; 6, *o*-cresol; 7, 3,5-xylenol; 8, benzene; 9, 2,3-xylenol; 10, chlorobenzene; 11, anisole; 12, 2,5-xylenol; 13, toluene; 14, phenetole; 15, methyl *p*-tolyl ether; 16, 2,6-xylenol.

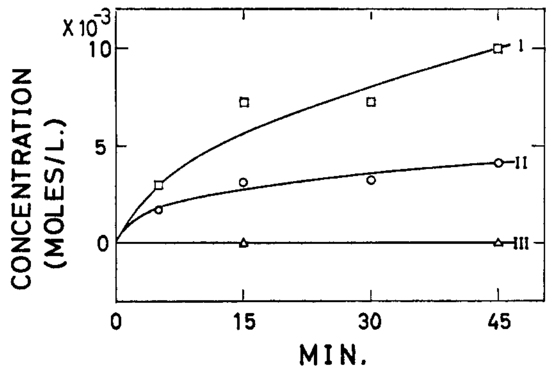

Figure 2.—Rate of formation of *o*-nitrosophenols under Baudisch conditions in methanol at 30°: I, *p*-cresol; II, phenol; III, benzene, anisole, phenetole, and methyl *p*-tolyl ether.

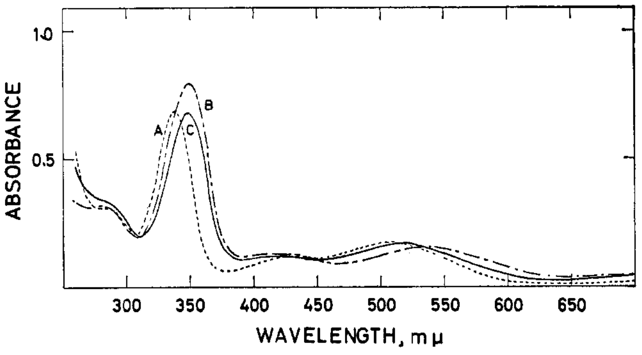

Figure 3.—Absorption spectra of copper(II) salt of A, 2-nitroso-*m*-cresol; B, 6-nitroso-*m*-cresol; and C, Baudisch reaction product of *m*-cresol in water.

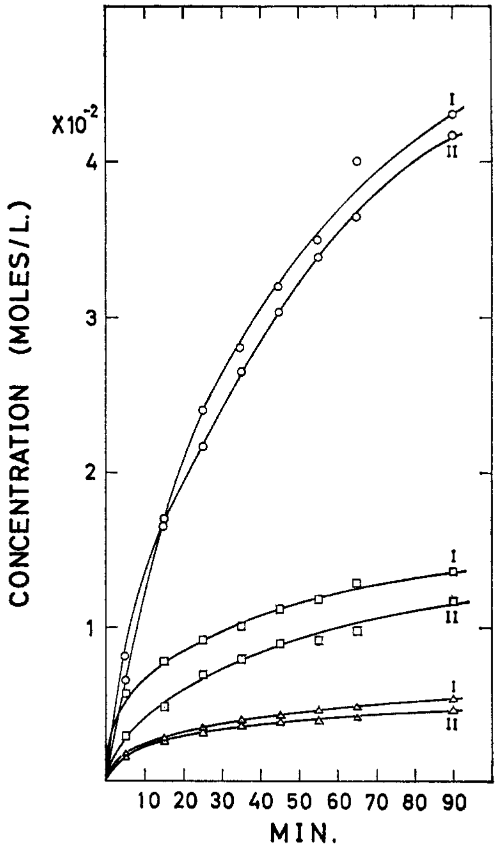

Figure 4.—Rate of formation of *o*-nitrosophenols under the condition of the Baudisch reaction at 30°: -○-, phenol; -△-, benzene; -□-, *p*-cresol; I, under a nitrogen atmosphere; II, in air.

TABLE II

o-NITROSOPHENOL FROM PHENOL AFTER 30 MIN AT 30°

Reagents	*o*-Nitrosophenol, × 10^{-3} moles/l.
$NaNO_2$–buffer[a]	0.88
$NaNO_2$–Cu^{2+}–buffer[a]	1.25
$NH_2OH \cdot HCl$–H_2O_2–buffer[a]	1.5[c]
$NH_2OH \cdot HCl$–H_2O_2–Cu^{2+}–buffer[a]	13.0
$NH_2OH \cdot HCl$–H_2O_2–Fe complex[b]–buffer[a]	5.1
$NH_2OH \cdot HCl$–H_2O_2–Cu^{2+} [d]	3.2

[a] A Walpole buffer (pH 2.5). [b] Sodium pentacyanoammine ferrate(II). [c] 1.8 × 10^{-3} moles/l. after 120 min. [d] Solvent, methanol.

clearly the exclusive activity of Baudisch's mixture in achieving *ortho* nitrosation.

As the copper(II) ion, in general, has a tendency to form complex ions with various amines and the pentacyanoammine ferrate(II) ion can exchange its coordinated ammonia molecule with amines, important clues to understanding the mechanism of the Baudisch reaction should be found from a consideration of the properties of a copper(II)–hydroxylamine complex. Further work on the entire reaction mechanism is in progress in our laboratories.

Experimental Section

Reagents.—Several of the reagents were prepared as shown in Table III according to directions in the literature. *m*-Cresol was purified according to the method of Brückner,[8] mp 10.5°. Reagent grade 30% hydrogen peroxide solution was obtained from Mitsubishi Chemical Co. and iodometric titration showed that this solution was 10.2 *M*. Other reagents were reagent grade and, if necessary, were used after further purification.

TABLE III

REAGENTS

Reagent	Mp (bp), °C	Ref	Lit. mp (bp), °C
Methyl *p*-tolyl ether	(175–177)	*a*	(176)
m-Chlorophenol	32.7	*b*	32–33
p-Nitrosophenol	139	*c*	133 dec at 144
2-Nitro-*m*-cresol	41.0	*d*	41
6-Nitro-*m*-cresol	55.0	*e*	56
Copper(II) hydroxide		*f*	
Sodium pentacyanoammine ferrate(II)		*g*	

[a] v. Auwers, *Ber.*, **47**, 3318 (1914). [b] M. A. F. Holleman and M. I. J. Rinkes, *Rec. Trav. Chim.*, **30,** 81 (1911). [c] J. L. Bridge, *Ann. Chem.*, **277**, 85 (1893). [d] J. Kenner and H. A. Turner, *J. Chem. Soc.*, 2341 (1928); H. H. Hodgson and H. G. Beard, *ibid.*, **127**, 498 (1925); G. P. Gibson, *ibid.*, **123**, 1269 (1923). [e] K. G. Blaikie and W. H. Perkin, *ibid.*, **125**, 307 (1924). [f] G. Brauer, "Handbuch der präparativen anorganische Chemie," Part 1, F. Enke Verlag, Stuttgart, 1954, p 756. [g] K. A. Hofmann, *Z. Anorg. Chem.*, **10**, 264 (1895).

Synthesis of *o*-Nitrosophenol.—A hydrogen peroxide solution (30%) (4 ml) was added to a solution of phenol (1 g), hydroxylamine hydrochloride (4 g), and sodium pentacyanoammine ferrate(II) (2 g) in 200 ml of water with 60 ml of petroleum ether (bp ~30–70°). This was stirred at room temperature. After 1 hr, the ether layer was separated and the water layer was repeatedly extracted with petroleum ether until the green color was scarcely found in the ether layer. The petroleum ether extracts of *o*-nitrosophenol were transferred to a flask and this flask was connected with an empty flask by means of T-tube fitted with a glass stopcock. After air was pumped out through the stopcock, the empty flask was cooled with a salt–ice mixture and the flask containing the extract was warmed with hot water. *o*-Nitrosophenol which was volatilized with the petroleum ether condensed in the ice-cooled flask. When the condensate was shaken with 0.5% copper(II) sulfate solution, the aqueous layer turned red. The visible and ultraviolet spectra of the aqueous layer were identical with those of the copper(II) salt of *o*-nitrosophenol which was obtained from *o*-nitrophenol.[9] The absorption maxima occurred at 339, 420, and 520 mμ.

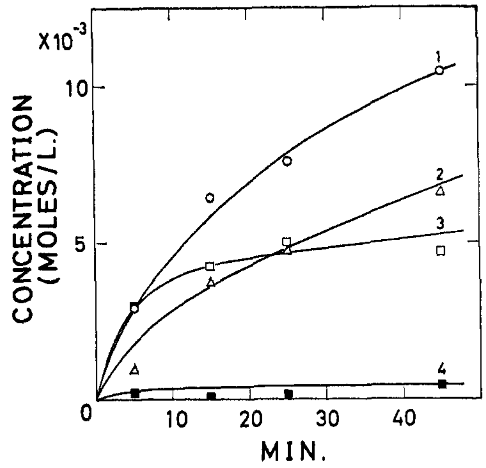

Figure 5.—Effects of various catalysts on the formation of *o*-nitrosophenol from phenol: 1, copper(II) oxide; 2, copper(II) nitrate; 3, sodium pentacyanoammine ferrate(II); 4, iron(II) sulfate.

Estimation of *o*-Nitrosophenol and *p*-Nitrosophenol.—An aqueous copper(II) sulfate solution of 1.0 × 10^{-2} *M* concentration was shaken with a solution of purified *o*-nitrosophenol in petroleum ether. The aqueous layer was separated from the ethereal layer after confirming that the ether still had a faint green color. The red aqueous layer was washed repeatedly with petroleum ether until no green color appeared in the petroleum ether. The resultant 1.0 × 10^{-2} *M* solution of copper(II) salt of *o*-nitrosophenol was diluted stepwise and at each step the absorbance of the solution at 339 mμ was measured with a Shimadzu spectrophotometer, Type QV-50. Beer's law was obeyed at concentrations below 6 × 10^{-4} *M;* this was satisfactory for the determination of the *o*-nitrosophenols. A calibration curve for *p*-nitrosophenol was prepared with the same apparatus using the absorption maximum at 302 mμ in ethanol.

Rate of Formation of *o*-Nitrosophenols in the Aqueous Mixture.—Benzene or various substituted benzenes (0.01 mole) were added to 198 ml of aqueous solution containing copper(II) nitrate (2.4 g, 0.01 mole) and hydroxylamine hydrochloride (1.4 g, 0.02 mole). The mixtures were stirred at 30° with *n*-hexane (20 ml) after 30% hydrogen peroxide (2 ml) was added. The reactions were conducted under a nitrogen atmosphere. After the addition of hydrogen peroxide, 1-ml aliquots of the reaction mixtures were pipetted out at intervals of ~10 min. The pipetted solutions were diluted 10 or 100 times for the colorimetric determination of the copper(II) salt of the *o*-nitrosophenols. The ultraviolet absorption maximum at 339 mμ was used.

Rate of Formation of *o*-Nitrosophenols in Alcoholic Mixtures.—The aromatic compounds (0.01 mole) were added to 195 ml of a methanolic solution containing copper(II) nitrate (2.4 g, 0.01 mole) and hydroxylamine hydrochloride (1.4 g, 0.02 mole). After addition of 30% hydrogen peroxide (5 ml), the mixtures were stirred at 30° under a nitrogen atmosphere. At intervals of ~15 min, 10-ml aliquots of the mixture were removed and were acidified with 6 *N* hydrochloric acid. They were then extracted with petroleum ether repeatedly. The petroleum extracts were shaken with aqueous 0.5% copper(II) sulfate solution and the water layers were diluted to 100 ml to determine the copper(II) salts of the *o*-nitrosophenols colorimetrically. The reaction proceeded in ethanol more vigorously than in methanol.

2-Nitroso-*m*-cresol and 6-nitroso-*m*-cresol were prepared by a method analogous to that which Baudisch used in the preparation of *o*-nitrosophenol from *o*-nitrophenol.[9] Zinc dust was added to a glacial acetic acid solution of 2-nitro-*m*-cresol and the

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(8) H. Brückner, *Z. Anal. Chem.*, **75**, 289 (1928).

(9) O. Baudisch, *Ber.*, **51**, 1058 (1918).

mixture was shaken vigorously. The zinc dust had been washed with dilute hydrochloric acid and water before use. After being acidified with 6 *N* hydrochloric acid, the mixture was extracted with petroleum ether. The petroleum ether extract was washed with twice-distilled water and shaken with an aqueous 5% copper(II) sulfate solution. The red copper(II) salt solution of 2-nitroso-*m*-cresol was obtained. By acidifying this solution, we obtained free 2-nitroso-*m*-cresol. The purification of this compound was carried out by repeated extraction with petroleum ether and salt formation with the copper(II) sulfate solution. The visible and ultraviolet spectra of the copper salt of 2-nitroso-*m*-cresol in water were determined on a Shimadzu recording spectrophotometer, Type SV-50A. 6-Nitroso-*m*-cresol was obtained by the same procedure from 6-nitro-*m*-cresol and the spectra of its copper(II) salt were determined on the same apparatus.

Specific Character of Catalysts.—Phenol (0.01 mole), hydroxylamine hydrochloride (0.02 mole), and the metal salt (0.01 mole) were dissolved into 198 ml of aqueous solution. Hydrogen peroxide (30%) (2 ml) was added to the mixture which was stirred at 30° under a nitrogen atmosphere. From the reaction vessel, 5 ml of the reaction mixture was pipetted out after 5, 15, 25, and 45 min had elapsed. The pipetted solution was acidified with 3 *N* sulfuric acid to obtain free *o*-nitrosophenol and was extracted with petroleum ether. The extract was treated with 0.5% copper(II) sulfate solution to obtain the copper(II) salt solution of *o*-nitrosophenol. After the solution was diluted to 100 ml, a colorimetric determination of *o*-nitrosophenol was conducted. Iron(II) sulfate, copper(II) nitrate, copper(II) hydroxide, and sodium pentacyanoammine ferrate(II) trihydrate were employed as metal salts. Since copper(II) hydroxide formed a dark green precipitate, 2 ml of concentrated hydrochloric acid was added before dilution of the solution to 198 ml. To prevent a side reaction, 0.05 mole, instead of 0.01 mole, of hydroxylamine hydrochloride was used in the reaction in which sodium pentacyanoammine ferrate(II) was employed as a catalyst.

Nitrosation of Phenol.—The following six reactions were conducted at 30° under a stream of nitrogen. The buffer solution used in several of the reactions was a Walpole buffer (pH 2.5) in which the resultant copper(II) salt of *o*-nitrosophenol was stable.

(1) Sodium nitrite (0.69 g, 0.01 mole) and phenol (0.47 g, 0.005 mole) were dissolved in 100 ml of the buffer solution and then the mixture was stirred.

(2) The same procedure as that above (1) was used, but copper(II) nitrate (1.24 g, 0.005 mole) was added to the solution.

(3) Hydroxylamine hydrochloride (0.69 g, 0.01 mole) and phenol (0.47 g, 0.005 mole) were dissolved in 100 ml of the buffer solution. The mixture was stirred with 1.0 ml of 30% hydrogen peroxide solution.

(4) The same procedure as that above (3) was used, but copper(II) nitrate (1.24 g, 0.005 mole) was added to the solution.

(5) An aqueous solution (100 ml) of hydroxylamine hydrochloride (0.69 g, 0.01 mole) and sodium pentacyanoammine ferrate(II) trihydrate (0.81 g, 0.0025 mole) was added to phenol (0.47 g, 0.005 mole). The mixture was stirred with 1.0 ml of 30% hydrogen peroxide solution.

(6) Hydroxylamine hydrochloride (1.39 g, 0.02 mole), phenol (0.94 g, 0.01 mole), and copper(II) nitrate (2.4 g, 0.02 mole) were dissolved in 195 ml of methanol. The mixture was stirred with 5 ml of 30% hydrogen peroxide solution.

In the case of reactions 1–5, 7 ml of concentrated hydrochloric acid was added to the reaction mixture 30 min after the reaction had begun. The acidified solution was extracted first with 10 ml of ethyl ether and then with 5 ml. The ethereal extracts containing the nitrosophenols were combined and examined by thin layer chromatography. In reaction 6, the reaction mixture was directly chromatographed.

Thin Layer Chromatography of Nitrosophenols.—Silica gel G (Merck, according to Stahl) (3 g) was suspended in 7 ml of 1% copper(II) sulfate solution and the suspension was supported on glass plates. The plates were allowed to stand for several minutes and activated at 105° in a oven. A small amount of sample solution containing the nitrosophenols was spotted on the chromatoplates and a unidimensional ascending technique was employed in a benzene–acetone (42:8) system. The copper(II) salt of *o*-nitrosophenol appeared as a pink zone near the starting point and the ascending *p*-nitrosophenol appeared as a yellow spot. The position of *p*-nitrosophenol was judged from observation of a spot of pure *p*-nitrosophenol developed on a corner of the same plate. After the chromatograms were air dried to remove the solvent, the copper salt of *o*-nitrosophenol and *p*-nitrosophenol were scraped separately into two weighing bottles and weighed. The copper salt of *o*-nitrosophenol on the silica gel was eluted with water several times and the combined solutions were diluted to a definite volume for colorimetric determination. A blank solution for colorimetry was prepared from a plate which was developed in the same jar without spotting. *p*-Nitrosophenol was eluted with ethanol and determined by a similar procedure.

Estimation of *o*-Nitrosophenol Produced by Various Reaction Conditions.—The same six reaction conditions as in the nitrosation of phenol were employed. After the reaction had proceeded for 30 min, 10 or 20 ml of the reaction mixture was pipetted from the reaction vessel and shaken with petroleum ether to extract *o*-nitrosophenol after acidification with concentrated hydrochloric acid. The extract was shaken with 0.5% copper(II) sulfate solution. For purification, the resultant copper salt solution was acidified with 6 *N* hydrochloric acid and a petroleum ether solution of the *o*-nitrosophenol produced was shaken with 0.5% copper(II) sulfate after being washed with water. The copper(II) salt solution was diluted to a definite volume to be estimated colorimetrically by means of the absorption maximum at 339 mμ.

Registry No.—*o*-Nitrosophenol, 13168-78-0; *p*-nitrosophenol, 104-91-6.