

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Mechanism of the Oxynitration of Benzene^{1,2}

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I. Introduction

In 1908 a patent was issued to Wolfenstein and Boeters³ for a procedure (hereafter called the oxynitration process) by which benzene is oxidized and nitrated to dinitrophenol or to picric acid by a solution of mercuric nitrate in nitric acid.

During World War II the over-all yield on the conversion of benzene to dinitrophenol by this process was increased (by research initiated by the NDRC) to about 85%.⁴ In connection with a general program related to the oxynitration process, we were asked to investigate the theory of the process. In the course of our research, we have established the general features of the mechanism beyond reasonable doubt. The process occurs in the following steps

(1) Presented at the September, 1946, meeting of the American Chemical Society.

(2) The work presented in this article is part of that performed for the National Defense Research Committee under contract OEMsr-875. Most of the material was submitted to the NDRC in a confidential report, OSRD 3154, which forms the basis of the present article.

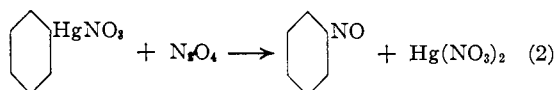
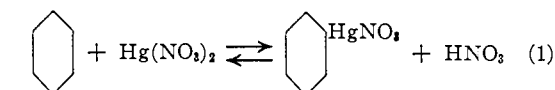
The research on oxynitration under the auspices of the NDRC was divided into three contracts, one under the direction of Professor Werner E. Bachmann at the University of Michigan, one under the direction of Professor Marvin Carmack at the University of Pennsylvania and a third under the direction of one of the authors at the University of Chicago. In addition, the reaction was investigated by Drs. D. C. Downing, J. H. Robertson and G. F. Wright for the National Research Council of Canada. All of these projects, except that at the University of Chicago, were largely concerned with practical preparative procedures. This division of the field was not, of course, absolute, and a good deal of work bearing upon mechanism was performed by groups other than the one in Chicago. (Conversely, we hope that some of our work on mechanism assisted the practical investigations.) Some of this additional work on mechanism will be presented in an article by Carmack, Baiser, Handrick, Kissinger and Specht to which appropriate references will be made. We have been informed that both Dr. Bachmann and Dr. Carmack intend also to publish the major part of their research, *i. e.*, that portion which deals with preparative methods.

We wish here gratefully to acknowledge the stimulation we received by conference with members of the other groups and by study of their reports. Two items especially assisted us in the development of the ideas set forth in this article. First, Carmack and his co-workers isolated a small quantity of phenylmercuric nitrate from an oxynitration mixture; their finding, as well as the older work of Desvergues (see ref. 6), strongly suggested phenylmercuric nitrate as a possible intermediate. Second, both Bachmann and Carmack obtained in the oxynitration process over-all yields somewhat higher than those predicted by the mechanism first advanced by us. This fact was among the important considerations which led us to the more complex mechanism hereafter described. This latter mechanism accounts for all the results obtained by any of the investigators.

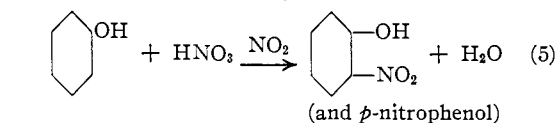
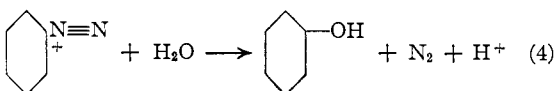
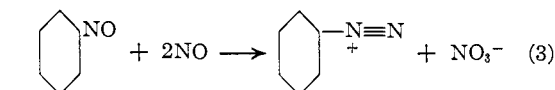
We wish also here to acknowledge the help and encouragement received from Dr. Ralph Connor who was Chief of Section 8.2 (later Chief of Division 8) while the present research was in progress, the help of Mr. Jack Bloom with some of the experiments, and the assistance of Dr. James K. Senior with the preparation of our NDRC reports.

(3) Wolfenstein and Boeters, *Chem. Abs.*, **2**, 489, 1861 (1908); **4**, 369 (1910); *Ber.*, **46**, 586 (1913).

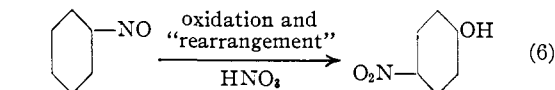
(4) (a) Carmack, Wagner, Baizer, Handrick, Kissinger and Specht, *THIS JOURNAL*, **69**, 785 (1947); (b) Bachmann, Chemerda, Deno and Horning, confidential reports to the NDRC.



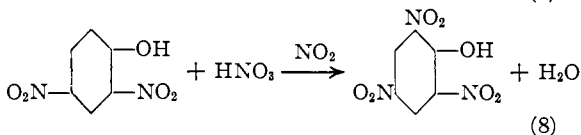
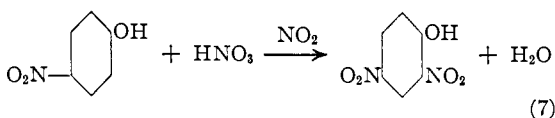
The nitrosobenzene formed in reaction (2) can then react in either of two ways.



or



The mononitrophenol formed either by reaction (5) or by reaction (6) is then further nitrated. (The particular isomers have been chosen only for illustration.)



In solutions where the concentration of nitrite is high and that of nitric acid low, reactions (3)–(5) take place. In solutions where the concentration of nitrite is low and that of nitric acid high, the oxynitration goes by way of reaction (6).

Many mechanisms previously have been postulated for the oxynitration process in question. Intermediates suggested include phenylmercuric nitrate,⁵ diphenyl mercury,⁶ tetranitrodiphenylmercury,⁶ nitrosobenzene,⁷ "nascent benzene,"⁸ hypothetical colored addition products of mercuric

(5) Downing and Wright, confidential Reports to the Canadian N. R. C.

(6) Desvergues, *Chim. & Ind.*, **22**, 451 (1929).

(7) Broders, private communication to Desvergues, ref. 6.

(8) Blechta and Patek, *Chem. Abs.*, **22**, 1961 (1928).

nitrate and benzene⁹ and others.¹⁰ (Wolffenstein and Boeters³ showed that nitrobenzene is a by-product, not an intermediate in the reaction.) Of the mechanisms previously advanced, that of Darzens¹¹ (which postulated phenyldiazonium nitrate as an intermediate) most nearly approaches the one here presented. The ideas of Darzens served as a guide for the early work on mechanism by all the N.D.R.C. groups. Since, however, experimental evidence in support of any mechanism has hitherto been lacking, none has yet been accepted.

The proof of mechanism here advanced includes the isolation of several intermediates. We identified the phenylmercuric ion as phenylmercuric chloride. When we used phenylmercuric nitrate as a starting material, we isolated nitrosobenzene. We identified the phenyldiazonium nitrate (equation 3) by its coupling product, *p*-dimethylaminoazobenzene. Wright and Downing⁵ had previously identified nitrogen (equation 4) as a reaction product. We have obtained evidence of the formation of the mononitrophenols (equations 5 and 6); the oxynitration can easily be carried out so that the chief product of the reaction is 2,4-dinitrophenol (equation 7).³

Although the isolation of these intermediates is reassuring, the proof of the mechanism is not (and cannot be) based on this evidence alone. In order definitely to establish the mechanism, it was necessary to prove that the rate of each reaction step is consistent with the final reaction products in the oxynitration of benzene and with the rates at which these products are formed. Further, this agreement must hold under a variety of experimental conditions.

We have measured the rates of the steps here postulated under widely different conditions of temperature and concentration of the reagents (including nitric acid and nitrite). Furthermore, the rates of several side reactions have been investigated, and the approximate amount of interference caused by each has been determined. The rate studies show that the mechanism here postulated is consistent with all the known facts.

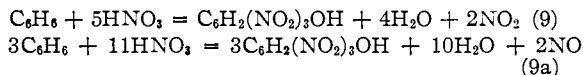
In the rest of this report, the reaction steps are taken up individually, and the method used to determine each reaction rate is outlined; the needed conclusions are then drawn. However, it may be well to state in advance a few of the more obvious predictions which can be made on the basis of the postulated mechanism. Evidently, if this mechanism is correct, the oxynitration reaction cannot occur in a medium which contains no nitrous acid or oxides of nitrogen, for reactions (2) and (3) involve oxides of nitrogen as reactants, and reactions (5), (7) and (8) involve such oxides as catalysts. We have established experimentally

that, in nitric acid which contains urea (and hence little or no nitrite) the oxynitration process does not occur. Instead, benzene is mercurated to form an equilibrium mixture of benzene, mercuric nitrate, and phenylmercuric nitrate. We have further shown that phenylmercuric nitrate, when dissolved in nitric acid containing urea, does not react to give nitrophenols; if, on the other hand, nitrite is added to a nitric acid solution of phenylmercuric nitrate, nitrophenols are rapidly formed.

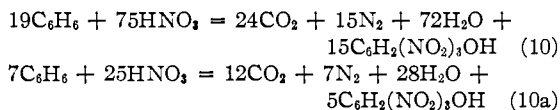
The choice of particular nitrogen oxides in equations (2), (3), (5), (7) and (8) is tentative, and equally plausible equations can be written involving other oxides.

II. The Stoichiometry of the Oxynitration

To the extent that the oxynitration proceeds by the rearrangement mechanism (equation 6), its stoichiometry is represented by that combination of equations (9) and (9a) which leads to the equilibrium mixture of nitric oxide and nitrogen dioxide in nitric acid.



To the extent that the oxynitration proceeds by the diazonium salt mechanism (equations 3, 4 and 5), its stoichiometry is represented by equations (10) and (10a).



The second of these equations (*i. e.*, 10a) was advanced by Carmack and his co-workers,^{4a} who pointed out the interesting fact that when oxynitration takes place by the diazonium salt mechanism there are two plausible stoichiometric equations for the reaction. Equation (10) is based on the assumptions that either benzene or nitrosobenzene is oxidized to carbon dioxide by nitric acid, and that the nitrous acid thus formed is consumed in the diazotization. Equation (10a) is based on the assumption that the oxidation of phenol furnishes the needed nitrous acid.

If the reaction proceeds according to equation (10), 79% of the benzene used can be converted to picric acid; if the reaction proceeds according to equation (10a), the maximum yield of picric acid is only 71%. On the other hand, if the reaction proceeds according to equations (9) and (9a), 100% yields of picric acid are at least theoretically possible.

III. The Mercuration of Benzene

Theoretical.—The mercuration of benzene with mercuric acetate is a familiar reaction.¹² Prior to the present investigation, Carmack and his co-workers had shown that mercuration with mercuric nitrate in the presence of ordinary dilute nitric acid gives a small yield of phenylmercuric

(9) Davis, Worrall, Drake, Helmkamp and Young, *THIS JOURNAL*, **43**, 594 (1921).

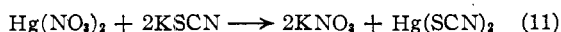
(10) See Vignon, *Bull. soc. chim.*, **27**, 547 (1920); Zakharov, *Chem. Abs.*, **22**, 3819 (1923); **25**, 4864 (1931).

(11) Darzens, private communication to Desvergues, ref. 6.

(12) Roeder and Blasi, *Ber.*, **47**, 2748 (1914).

nitrate.⁴ It is here shown that, in nitric acid containing urea, there is an equilibrium involving benzene, mercuric nitrate and phenylmercuric nitrate. The last of these was identified as phenylmercuric chloride; titration indicated that the yield of phenylmercuric ion was high.

The rates and equilibria of the mercuration of benzene in nitric acid solution were determined by titrating aliquot portions of the reaction mixture with thiocyanate. Mercuric ion reacts with two equivalents of thiocyanate, phenylmercuric ion, with one.



The equilibrium between benzene and mercuric nitrate is represented by the equation



It is, however, inconvenient to evaluate the equilibrium constant for this reaction, since the nitric acid is present partially in the ionized and partially in the un-ionized form. Moreover, a change from 20 to 50% nitric acid practically amounts to a change of solvent. Therefore, the data obtained are here presented in terms of the "apparent equilibrium constant"

$$(\text{Hg}(\text{NO}_3)_2)(\text{C}_6\text{H}_6)/(\text{C}_6\text{H}_5\text{HgNO}_3) = K' \quad (12)$$

where K' increases with increasing nitric acid concentration.

The rate of mercuration rises markedly with rise in the nitric acid concentration. Apparently the mercuration of benzene is acid catalyzed, for sulfuric acid also increases the rate, whereas nitrate ion is without effect. The data for the equilibrium and for the reaction rate are presented in Tables I and II, respectively. The first order rate constants for the disappearance of mercuric ion refer to the rates in nitric acid solutions saturated with benzene.

TABLE I

APPROXIMATE EQUILIBRIUM CONSTANTS FOR THE MERCURATION OF BENZENE AT 50°

$$(\text{Hg}(\text{NO}_3)_2)(\text{C}_6\text{H}_6)/(\text{C}_6\text{H}_5\text{HgNO}_3) = K'$$

% Nitric acid ^a	K' , m./liter
20	0.04 ± 0.02
30	.07 ± .03
40	.09 ± .02
50	.10 ± .01

^a The "per cent. nitric acid" throughout this paper refers to the per cent. acid used to make up the reaction mixture; in most cases this corresponded closely with the per cent. acid in the reaction mixture. When, however, the concentration of some material (*e. g.*, mercuric nitrate) was high, the per cent. acid in the reaction mixture was lower than that shown in the tables.

Second order velocity constants (expressed in $\text{min.}^{-1}(\text{m./liter})^{-1}$) can be obtained by dividing the first order constants by the solubility of benzene (expressed in moles/liter). Some of these solubilities (determined by Bachmann's method⁴)

TABLE II
THE RATE OF MERCURATION OF BENZENE

Concn. Hg(NO ₃) ₂ , m./liter	Concn. HNO ₃ , %	Concn. urea, m./liter	Added material	Concn.	T, °C.	k, min. ⁻¹
0.294	60	0.016			40	0.018
.0608	50	.16			40	.0038
.0603	50	.05			40	.0039
.292	50	.16			40	.0041
1.22	50	.16			40	.0056
0.297	50	.16			55	.013
.0598	40	.16			40	.0011
.295	40	.016			40	.0010
.0604	40	.08	NaNO ₃	1.65 m./l.	40	.0012
.292	40	.16	Al(NO ₃) ₃	0.027 m./l.	40	.0010
.292	40	.16			55	.0044
.0600	30	.16			40	.00045
.298	30	.016			40	.00037
.0602	30	.16	H ₂ SO ₄	20%	40	.0036
.298	30	.016	NaHSO ₄	2.2 m./l.	40	.00048
.291	30	.016			55	.0016
.0597	20	.16			40	.00014
.297	20	.016			40	.00016
.788	3	.016			40	.00006
.296	2	.016			40	.00003

are given in Table III. Evidently, the increase in the rate of mercuration with increasing nitric acid concentration is not primarily due to increased solubility of benzene in the stronger acid solution.

TABLE III

APPROXIMATE SOLUBILITY OF BENZENE IN HNO₃

% HNO ₃	Temp., °C.	Cc. benzene/ 100 cc. HNO ₃
60	40	1.18
50	40	0.64
50	55	.78
40	40	.44
40	55	.50
30	40	.32
30	55	.40
20	40	.28
2	40	.22
30 + 20% H ₂ SO ₄	40	.22

Comparison of these first order rate constants with those given in later sections and with the approximate over-all rate of oxynitration show that, in 50% nitric acid and at 55° (preparative conditions), the mercuration is the "slow step" which limits the rate of the entire process. In one liter of 50% nitric acid, the amount of benzene converted to phenylmercuric nitrate in three hours is about 0.7 mole, an amount which corresponds closely to the amount of dinitrophenol actually obtained in the oxynitration. Furthermore, the rate of mercuration increases with increase in the concentration of nitric acid, thus paralleling the observed increase in the rate of the oxynitration with increasing acid concentration. A detailed study of this relationship, much more precise than our original results, was made by Carmack.^{4a} He found that the rate of the production of dinitrophenol increased sevenfold (as one the rate of mercuration) as the nitric acid con-

centration is increased from 47.5 to 60%, and that the rate of formation of dinitrophenol was slightly less at each acid concentration than the rate of mercuration. It is, therefore, at once apparent why the oxynitration cannot be carried out successfully in very dilute nitric acid; the reasons why very concentrated nitric acid solutions cannot be used will be discussed later.

Experimental

The Equilibrium in the Mercuration of Benzene.—In order to follow the mercuration of benzene, a convenient analytical method was needed. The one finally selected was the direct titration of the reaction mixture with potassium thiocyanate; ferric ion was used as an indicator. Kolthoff and Lingane¹³ showed that this method is accurate for the determination of mercuric ion. Phenylmercuric thiocyanate is insoluble in water¹⁴ and blank tests showed that it could be quantitatively estimated in dilute nitric acid solution. Since mercuric ion combines with two equivalents of thiocyanate, whereas phenylmercuric ion combines with but one (equations 11 and 11a), the extent of the mercuration can be determined by titration. In actual practice, the mercuration mixtures were diluted with water before they were titrated; thus the concentration of nitric acid seldom exceeded 5%. The rate of mercuration in dilute nitric acid is so slow (see Table II) that no appreciable reaction takes place during titration.

Since the reaction between mercuric ion and benzene could be followed only in the absence of nitrite, urea was added to the reaction mixtures. It successfully prevented the "oxynitration" process. A test for nitrophenols was made by pipetting some of the reaction mixture into aqueous ammonia, which holds the mercury in solution as a complex ion. Lack of color in the ammoniacal solution showed that nitrophenols were absent even after a reaction mixture containing 40% nitric acid had been heated for forty hours at 50°. The validity of the test for nitrophenols depends upon the fact that these compounds are indicators, the alkaline solutions of which are bright yellow.

A possible objection to the use of urea lies in the fact that various mercuric salts form compounds with urea (2 moles salt to 1 mole urea).¹⁵ Although such compounds have never actually been prepared in strong acid solution, they may nevertheless be present in nitric acid. However, in the experiments here recorded, the concentration of urea was varied over a wide range (including concentrations very small compared with that of the mercuric ion) without appreciably affecting the rate of mercuration; it was therefore concluded that the urea in no way interfered with the accurate determination of the equilibrium position or the mercuration rate.

Solutions of benzene, urea and mercuric nitrate in nitric acid were sealed in glass ampoules. The free space in the ampoules was minimized, so that the benzene present in the vapor phase could be neglected. The ampoules were maintained at 50° in a thermostat; from time to time single tubes were removed, cooled and opened. The solutions were tested for nitrophenols (the tests were uniformly negative) and then titrated for phenylmercuric ion. Similar experiments were made on nitric acid solutions of phenylmercuric nitrate. Essentially the same equilibrium mixture was obtained from both sets of initial reactants. The precision of the determinations was greater in 40 or 50% acid than in 20 or 30% acid; measurements at these latter concentrations must be regarded as rather crude approximations.

The Rate of Mercuration of Benzene.—The rate of mercuration was determined by dissolving mercuric nitrate and urea in nitric acid of specified concentration, and then

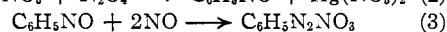
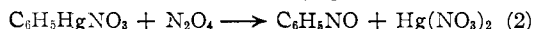
adding a large excess of benzene. The flask was closed with a ground glass stopper, and shaken vigorously in a thermostat held at 40°. From time to time, the flask was opened and a sample removed for titration. The loss of benzene during this operation was of no consequence, since the solution was at all times saturated with this compound. When such a reaction was partially complete, the reaction mixture was removed from the thermostat and an aqueous solution of sodium chloride added. The precipitated phenylmercuric chloride was collected; it melted at 247–248°. Whitmore¹⁶ gives 251° as the correct melting point.

The value of the equilibrium constant enters into the kinetic equation for a reversible reaction. Since, in the mercurations here discussed, the equilibrium constants are not known with precision, the rate constants recorded in Table II are obviously approximate. The error is not serious, however, for it is well known that an error in the value of an equilibrium constant does not materially affect the value of the velocity constants, provided these latter are determined from the initial rate. Since, in the experiments here recorded, the concentration of benzene did not change (the solution was always saturated), the equation for a reversible first order reaction was used. The velocity constants recorded in Table II were determined graphically from the first 10% of the reaction.

IV. The Diazotization Reactions

Theoretical.—In the course of the present investigation, it has been shown that when either phenylmercuric nitrate or nitrosobenzene is dissolved in dilute nitric acid and sodium nitrite added, phenyldiazonium nitrate is formed. This diazonium salt can be detected by coupling the material with an appropriate reagent such as R salt, β -naphthol, or dimethylaniline. When the last of these reagents is used, the yield of *p*-dimethylaminoazobenzene is 78%.

Reactions (2) and (3) (*cf.* page 773)



are somewhat analogous to reactions which have been known for many years. Bamberger¹⁷ converted diphenylmercury to nitrosobenzene and to phenyldiazonium nitrate by treating the mercury compound with oxides of nitrogen in chloroform solution. He also diazotized nitrosobenzene in acetic acid solution. Smith¹⁸ obtained nitrosodurene by treating a solution of tetramethylphenylmercuric nitrate with oxides of nitrogen.

A nitric acid solution of sodium nitrite contains HNO_2 , NO , NO_2 , N_2O_3 and N_2O_4 . Equations similar to (2) and (3) can be balanced almost regardless which of these reagents is selected. The tentative choice here suggested in equations (2) and (3) may therefore be in error.

The proof that nitrosobenzene is an intermediate in the diazotization of phenylmercuric nitrate depends (a) upon the isolation of nitrosobenzene from the diazotization mixture, and (b) upon the rate studies.

The diazotization rate was determined by removing aliquot parts of the reaction mixture, and coupling the diazonium compound present with

(13) Kolthoff and Lingane, *THIS JOURNAL*, **57**, 2377 (1935).

(14) Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1921, p. 177.

(15) Franklin, *THIS JOURNAL*, **29**, 35 (1907).

(16) Whitmore, *ref.* 14, p. 172.

(17) Bamberger, *Ber.*, **30**, 506 (1897); **51**, 634 (1918).

(18) Smith and Taylor, *THIS JOURNAL*, **57**, 2460 (1935).

R salt. The concentration of the azo dye thus formed was estimated colorimetrically.

Determination of the diazotization rates of phenylmercuric nitrate and of nitrosobenzene showed that, in dilute nitric acid, the diazonium salt is formed somewhat more slowly from phenylmercuric nitrate than it is from nitrosobenzene; this relation is a necessary but not a sufficient condition, if nitrosobenzene is an intermediate in the diazotization. The rate of diazotization of nitrosobenzene was measured in solutions of varying nitrite and nitric acid concentration. The reaction proved strictly first order with respect to the nitrosobenzene; the rate constants obtained are recorded in Table IV.

On the other hand, the diazotization of phenylmercuric nitrate in dilute nitric acid solution shows a marked induction period. This behavior may be quantitatively correlated with the assumption that the phenylmercuric nitrate is converted first to nitrosobenzene, and only subsequently to the diazonium compound. For, if such is the fact, then, when the rates of reaction (2) and reaction (3) are comparable, the rate equation for the formation of diazonium compound from phenylmercuric nitrate is

$$(DZ)/(P_0) = \frac{k_1 k_2}{k_2 - k_1} \left[\frac{e^{-k_2 t}}{k_2} - \frac{e^{-k_1 t}}{k_1} \right] + 1 \quad (13)$$

where (DZ) is the concentration of diazonium compound at the time t , (P_0) is the initial concentration of phenylmercuric nitrate, k_2 is the first order rate constant for the diazotization of nitrosobenzene, and k_1 the first order rate constant

TABLE IV

RATE OF DIAZOTIZATION OF NITROSOBENZENE

Concn. C_6H_5NO , m./liter	Concn. HNO_2 , ^a m./liter	Concn. HNO_3 , %	T , °C.	k , min. ⁻¹
0.0024	0.14	20	0	0.060
.0024	.28	20	0	.33
.0024	.28	30	0	.28
.0024	.28	40	0	.18
.0027	.16	20	25	.20
.0024	.07	20	25	.035

^a Throughout this paper the "concentration of nitrous acid" refers to that quantity determined by colorimetric analysis (see ref. 20); obviously it includes as nitrous acid the oxides of nitrogen in equilibrium with the nitrous and nitric acid.

TABLE V

RATE OF CONVERSION OF PHENYLMERCURIC NITRATE TO NITROSOBENZENE

Concn. HNO_3 , %	Concn. HNO_2 , m./liter	T , °C.	k , min. ⁻¹
20	0.075	0	0.003
20	.15	0	.006
20	.30	0	.020
20	.45	0	.053
30	.30	0	.22
40	.30	0	1.4
20	.15	25	0.05
20	.30	25	.065

for the conversion of phenylmercuric ion to nitrosobenzene. A short induction period similar to the one actually found may be predicted from equation (13). Using the values for the rate constants (independently determined, Table IV) for the diazotization of nitrosobenzene, the entire curve for the rate of diazotization of phenylmercuric nitrate was quantitatively fitted to equation (13) by a proper choice of one parameter, k_1 . The agreement in a particular experiment is shown in Fig. 1. This agreement (together with the isolation of nitrosobenzene) established nitrosobenzene as an intermediate in the diazotization of phenylmercuric nitrate in dilute nitric acid solution. It will later be shown that nitrosobenzene is also an intermediate when the oxynitration is carried out in concentrated nitric acid.

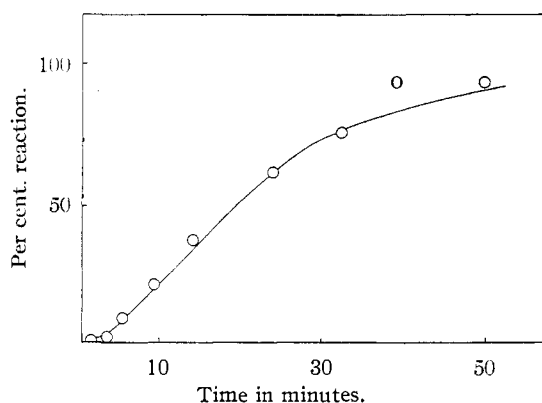


Fig. 1.—Diazotization of phenylmercuric nitrate: O, experimental, 20% HNO_3 and 0.16 m./l. HNO_2 ; solid curve for equation (13), with $k_1 = 0.05$ min.⁻¹ and $k_2 = 0.20$ min.⁻¹.

The rate constants for the diazotization of nitrosobenzene and for the conversion of phenylmercuric nitrate into nitrosobenzene in dilute nitric acid are given in Tables IV and V.

These figures show that the rate of diazotization of nitrosobenzene is practically independent of the nitric acid concentration, whereas the rate of conversion of phenylmercuric nitrate to nitrosobenzene increases rapidly as the concentration of nitric acid increases. Moreover, the rate of diazotization of nitrosobenzene depends on a high power (probably the square) of the gross nitrite concentration, whereas the rate of conversion of phenylmercuric nitrate to nitrosobenzene probably depends on the first power of the nitrite concentration.

In dilute (20 or 30%) nitric acid solution, essentially quantitative yields of diazonium compound are obtained from either nitrosobenzene or phenylmercuric nitrate. Where the nitrite concentration is high and the reaction rapid, the yield of coupling product is quantitative. This fact was demonstrated colorimetrically. However, where the concentration of nitrite is low and the diazotization correspondingly slow, it is necessary

to take account of the thermal decomposition of the diazonium compound formed during the reaction. When this correction is made, however, it becomes evident that all the nitrosobenzene (or phenylmercuric nitrate) is actually converted to diazonium compound.

By contrast, when either phenylmercuric nitrate or nitrosobenzene is diazotized in a solution of nitric acid more concentrated than 30%, the yield of diazonium compound falls below 100%, even if allowance is made for the thermal decomposition of the diazonium compound. The yield of diazonium compound is lowest when the nitric acid concentration is high (50%) and the nitrous acid concentration low. It will be shown (see Experimental Part) that, under these conditions, the nitrosobenzene is destroyed, and dinitrophenol produced, although neither phenyldiazonium nitrate nor phenol is formed in the solution. The nitrosobenzene undergoes the concurrent oxidation and rearrangement represented by equation (6) (see Section VI). It will here be shown that nitrous acid reacts on phenylmercuric nitrate to produce nitrosobenzene, even in concentrated nitric acid solution.

The rate of diazotization and the yield of diazonium salt can both be measured colorimetrically. The data obtained with phenylmercuric nitrate and with nitrosobenzene are recorded in Tables VI and VII.

TABLE VI
THE YIELD ON DIAZOTIZATION OF PHENYLMERCURIC NITRATE AND OF NITROSOBENZENE

Concn. HNO ₃ , %	Concn. HNO ₂ , m./liter	T, °C.	Concn. C ₆ H ₅ HgNO ₂ , m./liter	Yield, %	Concn. C ₆ H ₅ NO, m./liter	Yield, %
20	0.29	25			0.00125	100
30	.29	0	0.00635	100		
40	.73	0			.00064	100
40	.20	0	.00183	89	.00141	82
40	.20	0			.00070	81
40	.20	25			.00070	65
40	.041	0	.00186	13	.00073	12
40	.017	25			.00073	1
50	.72	0			.00064	44
50	.21	0			.00141	22
50	.19	0	.00081	15	.00073	17
50	.053	0			.00073	2
60	.050	25			.00073	1
60	.23	0	.00183	2	.00073	1

TABLE VII
THE RATE OF DIAZOTIZATION OF PHENYLMERCURIC NITRATE AND OF NITROSOBENZENE IN 40 AND 50% NITRIC ACID

Concn. HNO ₃ , %	Concn. HNO ₂ , m./liter	T, °C.	Concn. C ₆ H ₅ HgNO ₂ , m./liter	k, min. ⁻¹	Concn. C ₆ H ₅ NO, m./liter	k, min. ⁻¹
40	0.20	0	0.00090	0.13	0.00070	0.10
50	.20	0	.00090	.10	.00070	.10

Note that the yields of diazonium salt obtained from the two starting materials under the same

experimental conditions are essentially the same. The rate of diazotization of nitrosobenzene in 20% nitric acid is faster than the rate of conversion of phenylmercuric nitrate to nitrosobenzene under the same conditions. However, it has already been shown that the rate of conversion of the mercurial to nitrosobenzene increases with increasing nitric acid concentration. In 40% acid (*a fortiori* in 50% acid), the conversion of phenylmercuric nitrate to nitrosobenzene is so rapid that the former compound should diazotize at almost the same rate as the latter, and the experiment confirms this prediction. The fact that the yields and rates of diazotization of the two compounds are the same within experimental error indicates that nitrosobenzene is formed from phenylmercuric nitrate by the action of nitrous acid in concentrated nitric acid.

Experimental

Phenyldiazonium Nitrate.—Basic phenylmercuric nitrate^{18a} (0.485 g.) was dissolved in 50 cc. of hot 20% nitric acid; the solution was then cooled to 0°. Two cubic centimeters of 35% aqueous sodium nitrite solution was added, and the solution allowed to stand at 20° for half an hour. The mixture was then cooled to 0°, and the excess nitrite destroyed by gradually adding two grams of urea. When all the excess nitrite had been destroyed (as shown by the appearance of crystals of urea nitrate), the mixture was poured into 40 cc. of 25% sodium acetate solution. Half a gram of dimethylaniline was added. When the liquid turned red, aqueous sodium hydroxide was added to change the color to orange; the solution was then allowed to stand until coupling was complete. The *p*-dimethylaminoazobenzene was collected, and purified by dissolving it in dilute hydrochloric acid and reprecipitating it with excess sodium hydroxide. The azo compound was then recrystallized from alcohol; filtration of the hot alcoholic solution was necessary in order to remove an insoluble by-product. A total of 0.268 g. (78% yield) *p*-dimethylaminoazobenzene (m. p. 114–115°) was obtained. A mixture of this material with an authentic sample (m. p. 117°) melted at 117°.

The Isolation of Nitrosobenzene.—Broders⁷ claims to have obtained a small quantity of nitrosobenzene in an oxy-nitration of benzene. In the following experiments, the same compound was isolated from the product of the reaction between nitrite and phenylmercuric nitrate.

Basic phenylmercuric nitrate (1.0 g.) which had passed an 80-mesh sieve was dissolved at room temperature in 200 cc. of 20% nitric acid. The solution was transferred to a separatory funnel. Chloroform (25 cc.) which had been washed with water was added. Then a solution of 2.5 g. of sodium nitrite in 5 cc. of water was introduced, and the mixture shaken. After five minutes of occasional shaking, the green chloroform layer was withdrawn and 15 cc. of freshly washed chloroform added. The solution was again shaken, the chloroform withdrawn, and the process repeated periodically for an hour. Each chloroform extract was washed first with sodium chloride solution and then with water; if necessary, it was filtered. Finally the extracts were combined. The clear, green chloroform solution thus obtained contained nitrosobenzene, but the quantity could not be estimated colorimetrically. The chloroform solution was bright green, but a solution of pure nitrosobenzene in chloroform is blue-green. The two colors differ enough qualitatively to make matching impossible. The green color of the chloroform

(18a) Basic phenylmercuric nitrate, C₆H₅HgNO₂·C₆H₅HgOH, is commercially available, whereas the neutral salt, C₆H₅HgNO₂, is not. In the nitric acid solution these salts must be in equilibrium with each other.

extract here obtained is almost certainly due in part to an impurity, and not to nitrosobenzene itself.

The chloroform was removed from the extract at 150 mm. pressure by vacuum distillation through a short distilling column filled with glass helices. The residue was subjected to vacuum sublimation at 50° and about 1 mm. pressure. Most of the residue did not distill, but about 35 mg. of pale green nitrosobenzene collected on the receiver. The material melted at 64–67°; a mixture with an authentic sample of nitrosobenzene (m. p. 68°) melted at 66–68°. The yield was about 10% of the amount demanded by theory.

The preparation outlined above is open to the criticism that it was carried out in the presence of chloroform; it was then possible that the conversion of phenylmercuric nitrate to nitrosobenzene had taken place in the chloroform layer. A second method of preparation, in which no organic solvent was used, is described below.

Three grams of basic phenylmercuric nitrate was dissolved in 200 cc. of hot nitric acid which had previously been treated with 0.1 g. of urea. Since the nitric acid was nitrite-free, no reaction occurred during the solution process. The solution was cooled to room temperature, and an aqueous solution of sodium nitrite added. The resulting solution was 50% in nitric acid and 0.25 molar in nitrous acid. After 20 seconds, 200 g. of ice and 10 g. of urea were added to the reaction mixture. Then 365 cc. of 6 *N* sodium hydroxide and 45 cc. of 3.75 molar sodium acetate solution were introduced. The resulting faintly acid mixture was steam distilled. The yield of nitrosobenzene (m. p. 64–66°) was 180 mg. (18% of theoretical).

The Diazotization of Nitrosobenzene.—In order to determine the rate of diazotization of nitrosobenzene, any excess nitrous acid present must be destroyed before the diazonium compound can be coupled. If this is not done, the coupling component (dimethylaniline, naphthol, etc.) is nitrosoated. Considerable difficulty was encountered in this part of the investigation. When sulfamic acid was used to destroy excess nitrous acid, a large part of the diazonium compound was likewise destroyed. Even when urea was used, unusually low yields of diazonium compound were sometimes obtained. A more reliable method, which destroys the nitrous acid by converting it to sodium nitrite, is described below.

An aliquot portion of the solution of diazonium compound in nitric acid was withdrawn and pipetted into a cold solution of sodium hydroxide and sodium carbonate containing sufficient hydroxide almost to neutralize the acid. When necessary, the alkaline solution was partially frozen before use to keep the heat of the neutralization from raising the temperature of the mixture above 25°. An aqueous solution of R salt¹⁹ was immediately added. After coupling was complete, the solution was made strongly alkaline before it was matched in the colorimeter. The colorimetric standard was made by diazotizing a known amount of aniline, and coupling this solution with R salt in the manner indicated above. Aliquot portions of the original diazotizing solution were also withdrawn and diluted for a colorimetric determination of the concentration of nitrite.²⁰

Since the nitrous acid was destroyed by converting it to sodium nitrite, a coupling reagent which would react with phenyldiazonium salts in alkaline solution had to be used. Further, it was desirable that the resulting dye-stuff be freely soluble in water. These considerations prompted the use of R salt for colorimetric purposes. On the other hand, when it was desired to isolate the coupling product, dimethylaniline proved to be the most convenient reagent.

Phenyldiazonium nitrate cannot be quantitatively isolated from nitrosobenzene under any conditions because it is thermally decomposed in solution at an appreciable rate. Since the two consecutive reactions, diazotization of nitro-

sobenzene and decomposition of the diazonium salt are both of the first order, the expression for the fraction of diazonium compound present at any time, *t*, is

$$(DZ)/(A_0) = \frac{k_2}{k_3 - k_2} [e^{-k_2 t} - e^{-k_3 t}] \quad (14)$$

where (DZ) is the concentration of diazonium compound, (*A*₀) the initial concentration of nitrosobenzene, *k*₂ the rate of diazotization of nitrosobenzene, and *k*₃ the rate of decomposition of the diazonium salt.

The maximum yields which can (theoretically) be obtained at various values of the *k*₂/*k*₃ ratio may be derived from equation (14); they are given in Table VIII.

TABLE VIII

MAXIMUM YIELD OF DIAZONIUM COMPOUND	
<i>k</i> ₂ / <i>k</i> ₃	Yield, %
2	50
3	58
6	66
10	77
50	93

Within the limitations imposed by equation (14), the yields of diazonium salt obtained in 20 and 30% nitric acid solutions are nearly maximal. The rates of the conversion of phenylmercuric nitrate to phenyldiazonium nitrate and of the diazotization of nitrosobenzene have been previously discussed. The diazotization of phenylmercuric nitrate was carried out by the method used in the diazotization of nitrosobenzene.

The rate of diazotization and the rate of disappearance of nitrosobenzene in concentrated nitric acid were followed colorimetrically by essentially the method (coupling with R salt) previously described. However, some difficulties were encountered with the concentrated acid solutions, because the alkaline solutions obtained by neutralizing the reaction mixtures were quite yellow before any R salt had been added. This yellow color, which was probably caused by nitrophenols and phenyl-*p*-nitrosophenylhydroxylamine (see Section VII), prevented any quantitative determination of coupling product by visual colorimetric methods. However, the color could be estimated quite well in a Coleman Model 11 Spectrophotometer. This instrument has a very wide slit, admitting a 350 Å. spectral band; nevertheless, it is adequate for the purpose here in view. The yellow substances (see above) absorb strongly in the region around 4000 Å., but the absorption falls off sharply as the wave length increases; at 5250 Å. it is quite weak. On the other hand, the red dye formed by coupling the diazonium compound with R salt absorbs strongly at that wave length. The dye concentration could therefore be determined quite satisfactorily at 5250 Å.

V. The "Rearrangement" (Equation 6)

Theoretical.—The yield of diazonium salt obtained from either nitrosobenzene or phenylmercuric nitrate is negligible when these compounds are treated with 50% nitric acid and 0.05 normal nitrous acid. Nevertheless, there are several ways of showing that nitrosobenzene is unstable in such solutions. The first method depends upon the quantitative diazotization of nitrosobenzene in dilute nitric acid. A solution of nitrosobenzene in 50% nitric acid and nitrite was prepared; from this solution aliquot portions were withdrawn from time to time. The aliquots were added to an aqueous nitrite solution so adjusted that the final solutions obtained were not less than 0.35 molar in nitrous acid and not more than 30%

(19) Böeseken, Brandsma and Schoutissen, *Proc. Acad. Sci. Amsterdam*, **23**, 249 (1920).

(20) Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Company, New York, N. Y., 1936, p. 644.

in nitric acid. In these solutions, the remaining nitrosobenzene is quantitatively diazotized (see Section IV). The total quantity of diazonium compound formed is the sum of that formed in 50% acid and that formed in 30% acid. If the nitrosobenzene had undergone no reaction other than diazotization, the quantity of diazonium compound formed in the procedure described would have been equivalent to the amount of nitrosobenzene originally used (*i.e.*, the yield would be quantitative). Any alternative reaction of the nitrosobenzene in 50% acid would reduce the yield of diazonium salt. The extent of the alternative reaction can then be deduced by the amount by which the yield of diazonium salt falls below 100%. The rate of disappearance of nitrosobenzene can be most successfully determined where the diazotization in concentrated nitric acid solution is negligible, but the method described is serviceable even where such is not the fact.

TABLE IX
THE RATE OF "REARRANGEMENT" OF NITROSOBENZENE

Concn. C ₆ H ₅ NO	Concn. HNO ₃ , %	Concn. HNO ₂	T, °C.	k, min. ⁻¹
0.00073	40	0.00	0	0.0023
.00073	50	.00	0	.0082
.00073	50	.00	25	.097
.00073	50	.053	0	.034
.00073	50	.044	25	.26
.00070	50	.21	0	.12
.00073	60	.00	0	.072
.00140	60	.00	0	.074
.00073	60	.060	0	.070
.00073	60	.20	0	.083
.00091 ^a	60	.20	0	.073
.00068	60	.42	0	.080

^a C₆H₅HgNO₂ instead of C₆H₅NO.

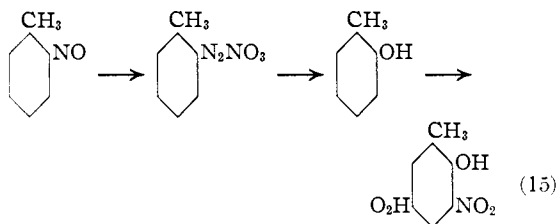
A second method of demonstrating the disappearance of nitrosobenzene from 50% nitric acid solution involves the preparation of dinitrophenol from phenylmercuric nitrate under experimental conditions such that little or no diazonium compound is formed. (In Section IV, it was proved that nitrosobenzene is formed from phenylmercuric nitrate.) Since the rates of destruction of the nitrosobenzene and phenylmercuric nitrate are known, the latter compound is added to the solution at a rate sufficient to maintain the concentration of nitrosobenzene at about 0.0005 molar. Under these conditions, the major side reaction of nitrosobenzene (see Section VII) is avoided. By this method, an 84% yield of 2,4-dinitrophenol of fairly good quality is obtained. This yield is considerably higher than would be possible if phenol were an intermediate in the reaction, for the highest yield obtainable from phenol under the experimental conditions here used is only about 70%.²¹ In connection with this latter reasoning, it is important to note that

(21) *Cf.*, however, Beaucourt and Hammerle, *J. prakt. Chem.*, **120**, 185 (1920).

Bachmann⁴ and Carmack⁴ obtained, by their special preparative procedures, over-all yields of dinitrophenol from benzene in excess of 80%. Clearly, then, neither phenyldiazonium nitrate nor phenol is an intermediate in the preparation of dinitrophenol by the "rearrangement" mechanism.

Next to be considered is the path by which nitrosobenzene is converted into dinitrophenol without formation of phenol as an intermediate. Various considerations suggested that the reaction involved a molecular "rearrangement,"^{21a} similar to that whereby phenylhydroxylamine is converted by acid to *p*-aminophenol.²² The reaction of nitrosobenzene with concentrated hydrochloric acid supports this hypothesis. Bamberger showed that, with this acid, nitrosobenzene reacts to form a mixture of products among which are 2,4-dichloroaniline and *p*-chlorophenylhydroxylamine, as well as *p,p'*-dichloroazoxybenzene and 2,4,6-trichloroaniline.²³ In these reactions a chlorine atom is introduced into the position in the ring para to the nitroso group, just as *p*-chloroaniline (not *p*-aminophenol) is produced in the reaction of phenylhydroxylamine with hydrochloric acid.²⁴ A "rearrangement" of nitrosobenzene in nitric acid solution might then be expected to introduce an hydroxyl group in the position para to the nitroso group. Such a reaction would be accompanied or followed by an oxidation which would produce a nitro group in the position formerly occupied by the nitroso group.

In order to test the hypothesis of a "rearrangement," *o*-nitrosotoluene²⁵ was prepared. This compound was found to behave much as does nitrosobenzene. It was almost quantitatively diazotized in 30% nitric acid in the presence of 0.15 molar nitrite; on the other hand, in 50% acid in the presence of 0.05 molar nitrite, it disappeared without undergoing diazotization. If the dual mechanism proposed (equations (3) and (6)) is correct, then *o*-nitrosotoluene, under the first conditions just cited, should be converted to 4,6-dinitro-*o*-cresol.



Under the second conditions, it should "re-

(21a) The word "rearrangement" is here used as it is used in discussing the "rearrangement" of phenylhydroxylamine. This usage does not imply that the oxygen atom which enters the benzene ring in the para position was originally attached to a nitrogen atom in either nitrosobenzene or phenylhydroxylamine.

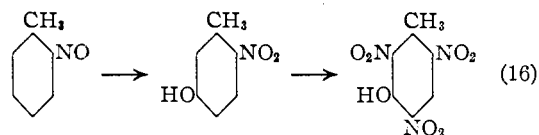
(22) Gattermann, *Ber.*, **26**, 1844 (1893); Bamberger, *ibid.*, **27**, 1347 (1894).

(23) Bamberger, Busdorf and Szolayski, *ibid.*, **32**, 210 (1899).

(24) Bamberger, *ibid.*, **28**, 245 (1895).

(25) Bamberger and Rising, *Ann.*, **316**, 257 (1901).

arrange"; the phenolic hydroxyl group, instead of replacing the nitroso group, should enter the ring in the position para to that group to form a nitrated derivative of meta cresol.



All these predictions were completely borne out by experiment. Trinitro-*m*-cresol has been previously reported among the products obtained in the oxynitration of toluene; reaction (16) probably explains its formation. (An alternative but less satisfactory explanation depends upon the fact that toluene, then mercurated, yields a mixture of ortho, para and meta derivatives.²⁶ The last of these might be converted to trinitro-*m*-cresol by a diazotization mechanism.)

The dual mechanism suggested for the reaction of nitrosobenzene with nitrous and nitric acid is consistent with the work of Downing and Wright,⁵ who studied the quantity of nitrogen formed during the oxynitration of benzene in 47% nitric acid. This quantity corresponded to about 0.5 mole per mole of picric acid formed. Downing and Wright operated at nitric acid and (presumably) nitrite concentrations which would make both of the suggested mechanisms important. Probably the mole fraction of nitrogen formed corresponded to the fraction of the nitrosobenzene diazotized.

Experimental

The Preparation of Dinitrophenol.—Dinitrophenol was prepared in such a way that the reaction took place almost exclusively through the "rearrangement" mechanism. Over a period of fifteen hours, 30 g. of basic phenylmercuric nitrate, ground to pass an 80-mesh sieve, was added to 2 liters of 50% nitric acid containing 0.04 molar nitrite. About 70 mg. of phenylmercuric nitrate was added every two minutes; the nitric acid solution was maintained at 25° and vigorously stirred. Every hour, a 2-cc. sample was withdrawn from the mixture and analyzed for nitrite²⁶; the concentration of nitrous acid was maintained at 0.04 m./liter by occasional additions of small amounts of sodium nitrite solution. At the end of the fifteen-hour period, the solution was heated to 50° for five minutes, and then allowed to stand in the ice-chest overnight. It was diluted with 1 liter of water, and extracted with seven 400-cc. portions of benzene. The benzene extracts were combined and concentrated to 150 cc.; they were then extracted with ten 10-cc. portions of a hot aqueous solution of diethanolamine.²⁷ When the diethanolamine solution was treated with concentrated hydrochloric acid and cooled, 14.5 g. of dinitrophenol precipitated. The tan colored product contained little, if any, picric acid; when thoroughly dried, it melted without prior softening at 110–111°. An additional 0.3 g. of very impure material (m. p. 78–84°) was obtained from the diethanolamine mother liquor. The benzene solution, after it had been extracted with diethanolamine, contained about 0.3 g. of an unidentified oil and about 0.1 g. of *p*-dinitrobenzene.

The Rate of Diazotization of *o*-Nitrosotoluene.—In a series of experiments similar to the ones conducted with

nitrosobenzene, *o*-nitrosotoluene was quantitatively diazotized in 40% (or weaker) nitric acid in the presence of 0.7 molar nitrous acid. The diazonium compound was coupled in alkaline solution with R salt. The color of the solution obtained was qualitatively and quantitatively identical with that of a solution formed by coupling diazotized *o*-toluidine with R salt. In 50% acid and 0.05 molar nitrite, on the other hand, *o*-nitrosotoluene yielded less than 5% of diazonium compound. The rate of disappearance of *o*-nitrosotoluene under these latter conditions was only about one-fourth the rate of disappearance of nitrosobenzene; preliminary results showed that the diazotization reaction was correspondingly slower. Bamberger has shown that, in sulfuric acid solution, *o*-nitrosotoluene dimerizes to form 2,3'-dimethyl-4'-nitrosodiphenylhydroxylamine.²⁸ No attempt was made to determine the rate of this dimerization, or the extent to which it might interfere with the reactions of *o*-nitrosotoluene.

Preparation of 2,4,6-Trinitro-*m*-cresol.—*o*-Nitrosotoluene (2 g.) was added in 70-mg. lots to 500 cc. of a 0.05 molar solution of nitrous acid in 50% nitric acid. The addition took place over a two-hour period during which the mixture was stirred and maintained at 35°. At the end of this period, the solution was heated to 95° for an hour; then it was cooled to room temperature and extracted with six 100-cc. portions of benzene. The benzene extracts were combined, concentrated to 100 cc. and then extracted with an aqueous solution of triethanolamine. When the triethanolamine solution was acidified, 2.67 g. (66% yield) of 2,4,6-trinitro-*m*-cresol was deposited. The crude material melted at 105–106°. After one recrystallization from aqueous alcohol, it melted at 108°; this melting point was not depressed by mixing the substance with 2,4,6-trinitro-*m*-cresol prepared by the nitration of *m*-cresol.

Preparation of 4,6-Dinitro-*o*-cresol.—*o*-Nitrosotoluene (5 g.) was introduced over a twenty-minute period into 500 cc. of a 0.25 molar solution of nitrous acid in 40% nitric acid. During this period, the mixture was stirred and maintained at 35°. Then the solution was heated to 50° for half an hour, cooled to room temperature and extracted with six 100-cc. portions of benzene. The benzene extracts were combined, concentrated to 100 cc. and then extracted with an aqueous solution of triethanolamine. When the triethanolamine solution was acidified with hydrochloric acid, a crude precipitate (m. p. 58–75°) separated. Most of this precipitate dissolved in hot ligroin, leaving behind some dark brown tar. When the ligroin solution was cooled, 4,6-dinitro-*o*-cresol (m. p. 83–85°) was obtained. The yield was 2.5 g. (31%). This material, after recrystallization from methanol, melted at 85–85.5°; the melting point was not depressed by the addition of 4,6-dinitro-*o*-cresol prepared by the nitration of *o*-cresol.

Alternatively, 4,6-dinitro-*o*-cresol was prepared from *o*-nitrosotoluene as follows. *o*-Nitrosotoluene (2 g.) was introduced over a one-hour period into 500 cc. of a 0.15 molar solution of nitrous acid in 20% nitric acid. During this period, the mixture was stirred and maintained at 35°. At the end of the hour, the solution was fortified with enough 70% nitric acid to make the resulting solution 40% in nitric acid. This solution was then heated at 50° for half an hour, cooled and worked up in the manner described for the previous preparation. The amount of 4,6-dinitro-*o*-cresol obtained was 40% of the theoretical yield; the crude material melted at 81–83°.

The low yields of 4,6-dinitro-*o*-cresol obtained in these preparations cannot be ascribed to incomplete diazotization of the *o*-nitrosotoluene; that they are related to the low yields obtained in the nitration of *o*-cresol was demonstrated by the following experiment. *o*-Toluidine (1.94 g.) was diazotized in a little cold 20% nitric acid. The solution of the diazonium salt was introduced over a period of one hour into 500 cc. of a 0.15 molar solution of nitrous acid in 20% nitric acid. The solution was then treated exactly as in the previous preparation. From the final

(26) Coffey, *J. Chem. Soc.*, **127**, 1029 (1925).

(27) This method of isolation was suggested by Wright and used by Bachmann.⁴

(28) Bamberger, Busdorf and Sand, *Ber.*, **31**, 1513 (1898).

ligroin solution, 1.50 g. of 4,6-dinitro-*o*-cresol (m. p. 83–85°) was obtained. This yield (42%) is only very slightly better than that obtained from *o*-nitrosotoluene.

4,6-Dinitro-*o*-cresol is destroyed under the experimental conditions necessary for the preparation of 2,4,6-trinitro-*m*-cresol. Consequently, the conditions of heating necessary to complete the two nitrations had to be different. Even in 20% nitric acid, 4,6-dinitro-*o*-cresol is destroyed by two hours heating at 95°; the rate of destruction increases with increasing acid concentration. Colorimetric tests for the presence of 2,4,6-trinitro-*m*-cresol can, however, be made by the method used for the determination of picric acid (see Section VI). When the reaction mixtures obtained in the preparation of 4,6-dinitro-*m*-cresol were thus tested, it was found that no 2,4,6-trinitro-*m*-cresol was formed in 20% nitric acid; the yields of this compound obtained in 40% acid were certainly less than 15% and probably much smaller.

VII. The Nitration of Phenol and the Nitrophenols

Theoretical.—The mechanism of nitration of phenol is still incompletely understood; some of the data have been submitted in a report to the NDRC.²⁹ Here only those facts essential to an understanding of the oxynitration reaction will be given. The results already presented demonstrate that when the oxynitration is carried out in dilute nitric acid, phenyldiazonium nitrate is formed. The decomposition of this salt is well known; the reaction product is probably phenol, although it could conceivably be phenyl nitrate. The rate of decomposition of phenyldiazonium nitrate in nitric acid solution has been found during the course of this investigation to be essentially the same as the rate previously reported³⁰ for dilute aqueous solution. The nitration of phenol can take place by at least two, and presumably by three, different mechanisms. In the industrial process, nitration is preceded by sulfonation.³¹ Alternatively, under proper conditions, the nitration can probably be carried out in such a way that the mechanism is the same as the mechanism for the nitration of nitrobenzene.³² However, in the oxynitration reaction, the nitration of any phenol formed as an intermediate is undoubtedly catalyzed by nitrite.³³ The best yields ever reported for this nitrite catalyzed nitration of phenol are in the neighborhood of 80%. The reaction is accompanied by the formation of an intense red coloring matter and some insoluble black tar. The structures of these by-products are still unknown.³⁴ Although the rate of nitration of phenol is not known precisely, it is clear^{34,29} that the rate is sufficiently rapid that it cannot in any way affect the over-all rate of the oxynitration process.

In view of the fact that about 20 to 30% of the phenol formed in the oxynitration is necessarily

(29) Westheimer, Bloom, Segel and Schramm, O. S. R. D. No. 4024.

(30) Cain and Nicoll *J. Chem. Soc.*, **81**, 1412 (1902).

(31) Olsen and Goldstein, *Ind. Eng. Chem.*, **16**, 66 (1924).

(32) Westheimer and Kharasch, *THIS JOURNAL*, **68**, 1871 (1946).

(33) Martinsen, *Z. physik. Chem.*, **50**, 385 (1905).

(34) Veibel, *Ber.*, **63**, 1577, 1582 (1930); *Z. physik. Chem.*, **B10**, 22 (1930).

destroyed, it is clear that the reaction which proceeds by way of the diazonium compound can never be quantitative. The preparation of picric acid or dinitrophenol in high yield depends on carrying out the oxynitration in such a way that little or no phenol is formed; under these conditions, the reaction proceeds almost exclusively by way of the "rearrangement" mechanism (reaction 6).

When the oxynitration proceeds by way of the diazonium salt mechanism, mononitrophenols are formed as intermediates. The method by which this fact has been established is outlined in the following experimental section.³⁵

The nitrations of the various nitrophenols in dilute nitric acid, like the nitration of phenol under similar conditions, are catalyzed by nitrite. The reactions are, however, much more efficient than the nitration of phenol; in fact, the yields of polynitrophenols are almost quantitative. In the present investigation, the rates of the nitration of several mono- and dinitrophenols were determined by a colorimetric method based upon the indicator properties of the nitrophenols in question.

The rate constants for the nitrations of the various nitrophenols, computed according to equation (17) are given in Tables X, XI, XII and XIII.

$$-d(\text{Nitrophenol})/dt = k'(\text{Nitrophenol}) \quad (17)$$

The values of k' so computed are functions of the nitrous acid concentration of the medium.

The following findings should be noted. (a) All the nitrations listed are nitrite-catalyzed. (b) At any particular concentration of nitric acid, all the nitration rates are about equally dependent on the nitrite concentration. (c) The increase in

TABLE X

THE RATE OF NITRATION OF <i>p</i> -NITROPHENOL					
<i>p</i> -Nitrophenol, m./liter	HNO ₂ , m./liter	HNO ₃ , %	<i>T</i> , °C.	<i>k'</i> , min. ⁻¹	
0.00314	0.081	60	30	0.055	
.00314	.030	60	30	.026	
.00314	.0048	60	30	.0038	
.00314	.0022	60	30	.0021	
.00314	.0007	60	30	.00060	
.00315	.031	50	0	.00009	
.00315	.048	50	30	.017	
.00315	.031	50	50	.011	
.00315	.017	50	50	.0078	
.00315	.0037	50	50	.0030	
.00315	.0017	50	50	.0012	
.00315	.031	40	30	.004	
.00315	.031	30	20	.0014	
.00315	.031	30	50	.014	
.00280	.143	30	50	.023	
.00280	.0058	30	50	.0053	
.00315	.031	20	50	.0023	
.00315	.031	10	50	.00041	

(35) See also McDonald and Calvert, *Chem. Abs.*, **13**, 2215 (1919).

TABLE XI

THE RATE OF NITRATION OF *o*-NITROPHENOL

<i>o</i> -Nitrophenol, m./liter	HNO ₃ , m./liter	HNO ₃ , %	T, °C.	<i>k'</i> , min. ⁻¹
0.00312	0.031	30	0	0.00005
.00312	.031	30	50	.069
.00312	.0054	30	50	.015
.00276	.00105	30	50	.0069
.00056	.0011	30	50	.0081
.00276	.029	30	50	.025
.00276	.102	30	50	.11
.00312	.031	20	50	.015
.00312	.031	10	50	.002

TABLE XII

THE RATE OF NITRATION OF 2,4-DINITROPHENOL

Concn.	Nitric acid, %	Concn. nitrite m./liter	T, °C.	<i>k'</i> min. ⁻¹
0.00125	50	0.026	50	0.00004

TABLE XIII

THE RATE OF NITRATION OF 2,6-DINITROPHENOL

Concn.	Nitric acid, %	Concn. nitrite m./liter	T, °C.	<i>k'</i> , min. ⁻¹
0.00102	50	0.027	50	0.0014
.00102	60	.0065	50	.0010
.00102	60	.029	50	.0034
.00102	60	.108	50	.011

the rate of nitration with increase in nitric acid concentration is about the same for all these compounds except phenol.

The rate of nitration of 2,4-dinitrophenol in 50% nitric acid (given approximately in Table XII) is very much less than the rate of mercuriation (given in Table II). This fact explains why 2,4-dinitrophenol can be obtained as the end-product in the oxynitration of benzene; only an additional prolonged heating will convert the dinitrophenol completely to picric acid.

A complete mechanism for oxynitration would specify which of the components of the nitric acid-nitrous acid system is responsible for the catalysis in the nitration of phenol (and which component converts C₆H₅HgNO₃ to C₆H₅NO, which converts C₆H₅NO to C₆H₅N₂NO₃). Preliminary research on this question was carried out by spectrophotometric analysis of the nitric acid-nitrous acid system. The concentrations of the yellow nitrogen dioxide and of the blue nitrogen trioxide could be separately established. Further and more precise research is necessary, however, before the problems stated above can be solved with certainty.

Experimental

The Colorimetric Method.—Ortho and para nitrophenols are indicators; their anions are very much more strongly colored than the corresponding acids. Reactions involving these nitrophenols may, therefore, be followed colorimetrically. Such a procedure can be successful only in the absence of other strong colors, specifically, the strong red-brown color which usually accompanies the oxynitration in 50% nitric acid. When this reaction is

carried out with a very dilute solution of phenylmercuric nitrate, and especially when the concentration of the nitric acid is less than 40%, the reaction mixture is sufficiently free from color; its slight tint is negligible compared with the strong yellow color of the nitrophenols in alkali.

In order to follow the nitration reactions, it is necessary to distinguish between mono- and dinitrophenols. This is done by taking advantage of the fact that the dinitrophenols are acids with ionization constants of about 1×10^{-4} , whereas the mononitrophenols have ionization constants of about 1×10^{-7} . Consequently, a sample of mono- and dinitrophenols in nitric acid can be analyzed for dinitrophenol by pipetting a sample of the mixture into a moderate excess of sodium acetate solution. In the resultant acetic acid-sodium acetate buffer, the dinitrophenols are largely ionized and highly colored, whereas the mononitrophenols are only slightly ionized and practically colorless. If a solution shows no color when poured into aqueous sodium acetate, the quantity of mononitrophenol present may be estimated from the color produced when excess alkali is added.

The rates of nitration of *o*- and *p*-nitrophenols were determined in the following manner. A standard solution of mononitrophenol and sodium nitrite in water or in very dilute sodium hydroxide was prepared. Five cubic centimeters of such a solution was added to 100 cc. of nitric acid in an Erlenmeyer flask; the solution was kept at constant temperature in a thermostat. To minimize loss of nitrite, the flask was closed with a "double stopper." This consisted of a waxed cork stopper which held a short piece of 8 mm. tubing; the tubing was in turn closed with a small waxed cork. From time to time the small cork was removed, and 2-cc. aliquots of the reaction mixture pipetted into measured quantities of sodium acetate solution. A standard solution of 2,4-dinitrophenol identical with the unknown in respect to the concentrations of hydrogen, acetate and nitrate ions had previously been prepared. The standard and the unknown were then compared in a Bausch and Lomb Duboscq type colorimeter.

To determine the loss of nitrous acid during an experiment, the reaction mixture was analyzed for nitrite,²⁰ both at the beginning and at the end of the reaction; in general, nitrite losses were small.

The nitration of *o*-nitrophenol is more complicated than that of para-nitrophenol, since in the first instance two compounds (2,4-dinitro and 2,6-dinitrophenol) are formed, whereas in the second instance, 2,4-dinitrophenol is the sole product. The 2,6-dinitrophenol is much more highly colored than the 2,4-compound, and is much more rapidly converted to picric acid. Experiment showed that the two isomeric dinitrophenols are formed at approximately equal rates from *o*-nitrophenol.

A rough but adequate method of overcoming these difficulties is as follows. The reaction is allowed to continue until the colors produced by two successive aliquots pipetted into standard volumes of sodium acetate solution are identical. This color is a maximum, for beyond the point mentioned, the highly colored 2,6- compound is very slowly converted into the less highly colored picric acid. Either of the two maximally colored solutions prepared from the two final aliquots is taken as the color standard for comparison with the solutions prepared from the aliquots previously withdrawn.

A colorimetric method for determining picric acid in mixtures containing dinitrophenols has also been developed. A 2-cc. sample of a solution of the mixed nitration products (in alkali or triethanolamine solution, if necessary) is introduced into 25 cc. of 10% nitric acid. In this strongly acid solution, only trinitrophenols (*e. g.*, picric acid) are ionized and colored. Their concentration can therefore be estimated colorimetrically. The rates of nitration of 2,4- and 2,6-dinitrophenols were determined by pipetting aliquots of the reaction mixture into water; in the dilute nitric acid solution thus formed, picrate is the only highly colored ion present.

When phenylmercuric nitrate was treated with a nitric acid solution of nitrite at 25°, the solution, if promptly

tested, was found to contain mononitrophenols but no dinitrophenols. If the solution was heated before being tested, dinitrophenols were found. Approximately a 65% yield of dinitrophenols was isolated by the diazotization of phenylmercuric nitrate in dilute nitric acid solution.

VII. The Side Reactions in the Oxynitration of Benzene

There are several side reactions which complicate the oxynitration of benzene. The most important of these probably are: (1) the formation of colored by-products from nitrosobenzene, (2) the formation of tetranitrodiphenylamine, (3) the formation of nitrobenzene by the direct nitration of benzene, (4) the formation of nitrobenzene from nitrosobenzene, (5) the formation of ortho and para dinitrobenzenes.

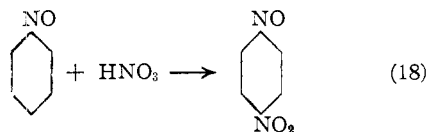
(1) **The Colored By-product.**—In nitric acid solution, nitrosobenzene reacts to form a colored substance. The color of the dark red solution resembles that of a completed oxynitration mixture. The conversion of nitrosobenzene to this colored material is slow in dilute but rapid in concentrated nitric acid. Further, the rate of conversion increases sharply with increasing concentration of nitrosobenzene; the reaction is, therefore, of kinetic order greater than one. The total amount of color produced from dilute solutions of nitrosobenzene is less than that formed from concentrated solutions of this compound. It seems probable that the yield of useful products obtainable from nitrosobenzene formed during oxynitration in concentrated nitric acid is limited by the amount of nitrosobenzene consumed by the side reaction in question. The course of the reaction has not been sufficiently well determined to allow definite estimates of rate constants to be made. It is clear, however, that its rate is competitive, in concentrated nitric acid, with that of the "rearrangement." It seems logical to assume that one of the products formed (at least temporarily) is phenyl-*p*-nitrosophenylhydroxylamine, which is formed quantitatively by the action of concentrated sulfuric acid on nitrosobenzene.²³

(2) **Tetranitrodiphenylamine.**—This product was isolated from the reaction mixture and identified by Bachmann and co-workers.⁴ This compound has also been obtained by us in small yield by the action of nitric and nitrous acids on phenyl-*p*-nitrosophenylhydroxylamine.

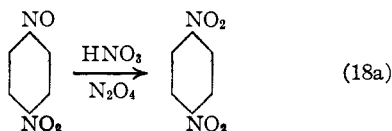
(3) **The Nitration of Benzene.**—The direct nitration of benzene is an important side reaction in the oxynitration. The kinetics of this reaction under appropriate conditions have, however, not yet been investigated.

(4) **Nitrobenzene from Nitrosobenzene.**—Bachmann and his co-workers showed that nitrobenzene can result from the treatment of nitrosobenzene with nitric acid.

(5) **The Nitration of Nitrosobenzene.**—Two of the minor by-products of the oxynitration are *o*- and *p*-dinitrobenzene.^{5,6} Presumably, these by-products are formed by the nitration of nitrosobenzene.



The *o*- or *p*-nitronitrosobenzene is then oxidized to dinitrobenzene.



The Mercuration of Phenol.—It seemed possible that the mercuric salts present in the oxynitration mixture might interfere with the nitration of any phenol formed as an intermediate. This, however, proved not to be the fact. The rate of mercuration of phenol was measured in nitrite free (urea-containing) solutions of nitric acid. This rate, except in very dilute nitric acid, proved to be much lower than the rate of nitration in similar solutions containing nitrite.

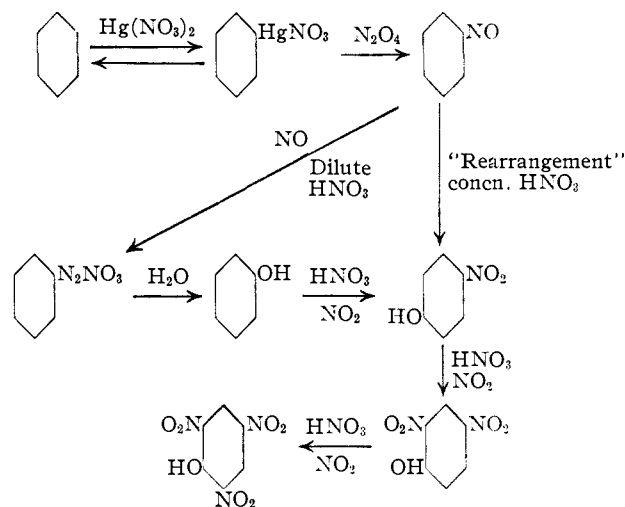
It was also shown that mercuric nitrate in no way affects the rate of nitration of phenol.

TABLE XIV
THE RATE OF MERCURATION OF PHENOL

Concn. HNO ₃ , %	Concn. C ₆ H ₅ OH and of Hg(NO ₃) ₂ , m./liter	T, °C.	k, min. ⁻¹ (m./l.) ⁻¹
5	0.309	0	0.030
10	.309	0	.050
10	.309	25	.80
22	.309	0	.10
34	.309	0	.40

Summary

A mechanism has been established for the process in which benzene is oxidized and nitrated to picric acid by a solution of mercuric nitrate in nitric acid. This process takes place in the following steps.



The supporting evidence here obtained for this mechanism includes the identification of the following intermediates: phenylmercuric ion, nitrosobenzene, phenyldiazonium ion and mononitrophenol. The hitherto unreported "rearrangement" of nitrosobenzene has been established by studying the analogous reaction of *o*-nitrosotoluene, which, under appropriate conditions, yields trinitro-*m*-cresol. This reaction proves that an hydroxyl group enters the benzene ring para to the nitroso group.

The kinetic studies here presented are, however, the most convincing evidence for the mechanism postulated. The rate of each individual step, and the rates of several side reactions have been determined. It was shown that in the presence of urea, only the mercuration takes place;

the other reactions occur only in the presence of nitrite. The mercuration has been shown to be the slow step in the whole oxynitration process; the rate of formation of phenylmercuric nitrate is about equal to the rate of formation of dinitro-

phenol. Since the rates of the other steps in the process and the yields obtained in those steps agree with the mechanism postulated, this mechanism becomes extremely probable.

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The Oxynitration of Benzene. I. Studies Relating to the Reaction Mechanisms¹

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"Oxynitration" is a process by means of which aromatic hydrocarbons, particularly benzene, can be oxidized and nitrated to nitrophenols in a single operation. The oxynitrating reagent consists of a solution of mercuric nitrate in aqueous nitric acid. For the preparation of 2,4-dinitrophenol from benzene a number of previous investigators have recommended the use of 50–55% nitric acid, 0.2 to 0.5 *M* mercuric nitrate and temperatures in the range of 25 to 65°, although wider variations of all of these variables have been explored.

At the beginning of the present investigation of the oxynitration process, the unproved reaction mechanism proposed by Darzens^{4,5} served as a useful guide to further studies, both of the mechanism and of practical means for the production of nitrophenols. According to Darzens, the oxynitration of benzene involves the following intermediate reactions: benzene → phenylmercuric nitrate → benzenediazonium nitrate → phenol → mononitrophenol → 2,4-dinitrophenol. If the re-

action conditions are sufficiently severe, some of the dinitrophenol may be further nitrated to picric acid.

Intermediates.—Darzens⁴ (as quoted by Desvergnès) suggested that phenylmercuric nitrate is formed in the first step by the direct mercuration of the benzene; in subsequent steps the action of nitrogen oxides on the mercury derivative regenerates the catalyst simultaneously with the formation of other reactive intermediates. No experimental evidence for the formation of phenylmercuric nitrate was cited by Desvergnès. Blechta and Pátek⁶ also postulated phenylmercuric nitrate as the first intermediate in oxynitration, but differed from Darzens in suggesting that the action of acid upon the mercurial compound regenerates benzene, which, in the instant of regeneration, exists in an activated or "nascent" form susceptible to oxidation by the nitric acid.

Definite evidence for the presence of phenylmercuric compounds in the oxynitration reaction mixtures was obtained in the present investigation by the use of somewhat more dilute nitric acid (35%) than is customary for oxynitration and by a decrease in the reaction time. Under these conditions phenylmercuric salts accumulated in the solution and were isolated as the crystalline basic phenylmercuric nitrate, $C_6H_5 \cdot HgNO_3 \cdot C_6H_5 \cdot HgOH$.⁷

The addition of solid phenylmercuric salts to 50% nitric acid under conditions approximating those of the usual oxynitration procedure resulted in the rapid formation of 2,4-dinitrophenol and small amounts of *p*-dinitrobenzene, in about the same proportions as in the oxynitration of benzene. The rate of addition of the phenylmercuric salt to the nitric acid influenced the yield of 2,4-dinitrophenol strikingly. When the phenylmercuric salt was added in a single portion, only low yields of the desired product were obtained, and a considerable proportion of highly colored, poorly defined by-products also resulted. The yield and quality of dinitrophenol were improved markedly when the phenylmercuric salt was divided into

(1) The work described in this article is part of that performed under Contract OEMsr-646, recommended by the National Defense Research Committee, between the University of Pennsylvania and the Office of Scientific Research and Development. Other contract groups at the University of Michigan, under Professor W. E. Bachmann, and the University of Chicago, under Professor F. H. Westheimer, participated in the investigation of the oxynitration reaction. Most of the work on reaction mechanism was carried out at the University of Chicago, while the work of the other two groups was concerned primarily with the development of practical methods for the preparation of nitrophenols. Simultaneously, the oxynitration reaction was studied by a group under Professor George F. Wright at the University of Toronto and another group under Professor Raymond Boyer at the University of Montreal. The reader should consult the paper by Westheimer, Segel and Schramm (ref. 3) for a full discussion of the mechanism and for a review of earlier work.

The results of the investigations of the preparative procedures for oxynitration will be presented at a later time.

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(3) Westheimer, Segel and Schramm, *THIS JOURNAL*, **69**, 773 (1947).

(4) Darzens, private communication of December 8, 1914, to Desvergnès (ref. 5).

(5) Desvergnès, *Chimie & Industrie*, **22**, 451 (1929).

(6) Blechta and Pátek, *Z. ges. Schiess- u. Sprengstoffw.*, **22**, 314 (1927).

(7) Pyman and Stevenson, *Pharm. J.*, **133**, 269 (1934); *C. A.*, **28**, 6944 (1934).