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 dinitrophenol. 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 Mechanisms[1]

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

Intermediates.—Darzens[4] (as quoted by Desvergnes) 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 Desvergnes. Blechta and Pátek[6] 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, $C_6H_5HgNO_3 \cdot C_6H_5HgOH$.[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

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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 Desvergnes (ref. 5).

[5] Desvergnes, *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).

small portions and added over an extended reaction period; the yield increased as the size of the individual increments was decreased and the time of addition was increased. Similar results were obtained with either phenylmercuric acetate or basic phenylmercuric nitrate.[8] The reaction mixtures resembled in every way those of typical oxynitration runs except that only small amounts of nitrobenzene were formed.

Benzene was found to react with mercuric nitrate even in dilute nitric acid solution (of the order of 5% or less), although more slowly than in stronger nitric acid. In such dilute acid little or no nitrophenolic material was produced, but, instead, mixtures of solid mono- and polymercurated benzene derivatives of indefinite composition resulted.[9] The extent of mercuration was studied by cleavage of the mixture of solid products with bromine water. The resulting mixture of brominated benzene derivatives was separated on the basis of boiling range into mono-, di-, tri- and tetrasubstituted bromobenzenes. From the weights of the fractions the approximate mole percentage composition of the mercuration mixture was estimated to be as follows: 53% monomercurated, 38% dimercurated, 7% trimercurated and 2% tetramercurated. Among the bromination products, bromobenzene, *p*-dibromobenzene and 1,3,5-tribromobenzene were isolated, and a small amount of a solid which was tentatively identified as 1,2,4,5-tetrabromobenzene. The cleavage of phenylmercuric salts with bromine water is considered to involve the direct replacement of the substituent mercuri groups with bromine atoms, and has been used in the determination of structure of mercury compounds.[10,11] It seems justifiable to assume on the basis of earlier work that the polybrominated products are formed from similarly substituted polymercurated benzene derivatives. The separation of individual isomers was not quantitative; it is probable that other isomers were present in the residual liquid fractions of bromo compounds.

Final proof that phenylmercuric nitrate is an intermediate in the oxynitration of benzene was provided by Westheimer, Segel and Schramm[3] in their demonstration that the rates of mercuration of benzene in nitric acid agree well with the overall rates of oxynitration over a wide range of concentrations of nitric acid. Their finding that all of the steps of oxynitration except the mercuration are inhibited by the presence of urea in the nitric acid provided a convenient means for the study of the kinetics of the mercuration step.[12]

The second step of the reaction sequence postulated by Darzens,[4] the conversion of phenylmercuric nitrate into benzenediazonium nitrate by the action of nitrogen oxides, was shown to operate in the oxynitration procedure by Westheimer and co-workers, who isolated a solid derivative of the diazonium compound and showed that the rates of formation and yields of the diazonium compound obtainable in concentrations of nitric acid up to 40% tend to support Darzens' reaction mechanism.

The reports of the cleavage of arylmercury compounds by nitrogen oxides to yield arylnitroso derivatives[13,14] and the long-known conversion of arylnitroso compounds to aryldiazonium salts[13,14,15] suggested to us the possibility that nitrosobenzene is an intermediate in the diazotization step of oxynitration. The isolation of nitrosobenzene from oxynitration mixtures has been claimed by Broders,[16] but it appears that Broders considered the nitrosobenzene merely to be the source of the by-products, nitrobenzene and *p*-dinitrobenzene, rather than of the major product, dinitrophenol, since he postulated 2,4,2′,4′-tetranitrodiphenylmercury as the precursor of dinitrophenol.

We found that nitrosobenzene reacts with nitrogen oxides and nitric acid in the absence of mercuric nitrate to form 2,4-dinitrophenol in good yield.[17] Simultaneously, Westheimer, Segel and Schramm[3] reported the isolation of nitrosobenzene from the reaction of basic phenylmercuric nitrate and nitrous acid, and in subsequent kinetic studies demonstrated conclusively that nitrosobenzene is an intermediate in the oxynitration of benzene.

The Stoichiometry of the Oxynitration Reaction.—Since the fate of the benzene and the consumption of nitric acid were matters of practical interest, considerable attention was

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[8] (a) A convenient procedure which differs from previously published methods (refs. 8b-d) was developed for the conversion of phenylmercuric acetate into the basic phenylmercuric nitrate. The method involves the addition of an ammoniacal solution of phenylmercuric acetate to an excess of strong nitric acid; (b) Woollett and Coulter, THIS JOURNAL, **56**, 1922 (1934); (c) U. S. Patent, 2,131,008; *C. A.*, **32**, 9403 (1938); (d) U. S. Patent 2,173,845; *C. A.*, **34**, 451 (1940).

[9] Dimroth, *Ber.*, **32**, 760 (1899), noted the reaction of aqueous mercuric nitrate with benzene at 110–115° but did not further examine the nature of the reaction products. Kobe and Lueth, *Ind. Eng. Chem.*, **34**, 309 (1942), describe a procedure for the monomercuration of benzene in acetic acid which is designed to minimize the formation of polymercurated products.

[10] Coffey, *J. Chem. Soc.*, **127**, 1029 (1927).

[11] Barduhn and Kobe, *Ind. Eng. Chem.*, **38**, 247 (1946).

[12] We have verified the good agreement between the rates of mercuration calculated from the rate constants of Westheimer, Segel and Schramm and the rates of formation of 2,4-dinitrophenol in a large-scale laboratory apparatus designed for the continuous operation of the oxynitration reaction under approximately constant reaction conditions.

We have also carried out the continuous mercuration of benzene in nitric acid containing urea and have by this direct method conveniently obtained good yields of phenylmercuric salts uncontaminated with nitrophenols. Data on these experiments will be published later with the description of the apparatus for continuous oxynitration.

[13] Bamberger, *Ber.*, **30**, 512 (1906).

[14] Smith and Taylor, THIS JOURNAL, **57**, 2461 (1935).

[15] (a) Bamberger, *Ber.*, **51**, 634 (1918); (b) Weselsky, *ibid.*, **8**, 98 (1875); (c) Jaeger, *ibid.*, **8**, 894 (1875); (d) Ikuta, *Ann.*, **243**, 283 (1888); (e) Hantzsch, *Ber.*, **35**, 893 (1902).

[16] Broders, "Travaux effectués au laboratoire de recherches de la Poudrerie de Saint-Fons," (Saint Fons, 17 February, 1919), cited by Desvergnes (ref. 5).

[17] The conversion of nitrosobenzene to dinitrophenol on a preparative scale was also investigated by Bachmann and co-workers.

given to the stoichiometry of the oxynitration process, and the results proved to have a direct bearing on the problem of the mechanism.

Two somewhat different interpretations of the stoichiometry of the modified Darzens reaction sequence involving phenylmercuric nitrate, nitrosobenzene, benzenediazonium nitrate and phenol as intermediates were proposed by Westheimer and co-workers and by the group at the University of Pennsylvania. In both equations the assumptions were implicit that nitrogen oxides are required for some of the intermediate steps and that these can only be supplied by reduction of nitric acid at the expense of oxidation of part of the organic material. The assumption of Westheimer, Segel and Schram that benzene, or an intermediate preceding benzenediazonium nitrate in the sequence, is oxidized to produce the nitrogen oxides leads to the following equation for the production of dinitrophenol

$$19C_6H_6 + 60HNO_3 = 24CO_2 + 57H_2O + 15N_2 + 15C_6H_3(NO_2)_2OH^{18a} \quad (1)$$

The alternative equation proposed independently by the Pennsylvania group involves the assumption that phenol, benzenediazonium nitrate or some other substance derived from the diazonium salt is oxidized to carbon dioxide and nitrogen, with the corresponding reduction of an equivalent quantity of nitric acid to produce the nitrogen oxides needed

$$7C_6H_6 + 24HNO_3 = 12CO_2 + 23H_2O + 7N_2 + 5C_6H_3(NO_2)_2OH^{18b} \quad (2)$$

On the basis of equation 1 a maximum yield of 79% of dinitrophenol (based upon benzene) would be expected; four moles of nitric acid would be consumed in the formation of each mole of the major product, and one mole of free nitrogen would be evolved. Equation 2 leads to the prediction of a maximum yield of 71% of dinitrophenol based upon benzene, the consumption of 4.8 moles of nitric acid per mole of dinitrophenol formed, and the evolution simultaneously of 1.4 moles of nitrogen.

The finding of Downing and Wright[19] that approximately 0.45 mole of nitrogen and 0.3 mole of nitrous oxide was evolved for each mole of picric acid produced in their oxynitration process neither excluded nor completely supported the Darzens mechanism as an important route to the nitrophenols.

On the basis of the diazonium mechanism, which requires that sufficient oxides of nitrogen be generated by destructive oxidation of organic material to convert phenylmercuric nitrate to nitrosobenzene and nitrosobenzene to benzenediazonium nitrate, it was thought that some of the destructive oxidation of benzene (or intermediates derived from benzene) might be avoided if oxides of nitrogen were to be conducted into the reaction mixture from an external source. In a number of batch oxynitration runs various attempts were made to realize this expectation by the introduction of nitrogen dioxide, nitric oxide, or mixtures of nitrogen oxides from a separate generator. None of these was successful; in fact, the yields in most cases were decreased markedly below the yields that were obtained under comparable conditions without the addition of excess oxides, and at the same time the formation of intensely red-colored, tarry by-products was promoted. Other modifications involving the generation of oxides within the reaction mixture, by addition of sodium nitrite or by addition of very readily oxidizable organic substances such as hydroquinone, all failed to improve the yield and generally had the opposite effect. It was concluded that high concentrations of nitrogen oxides within the oxynitration mixture are detrimental to the yields of nitrophenolic products.

In the later experiments on the preparation of dinitrophenol by both batch and continuous procedures, it was observed that the yields of dinitrophenol based upon benzene (with allowance for the benzene lost by evaporation and in the formation of neutral nitro compounds) exceeded the upper limit of 79% set by equation 1.

The discovery by Westheimer, Segel and Schramm of a second path by which nitrosobenzene is converted into dinitrophenol explains the failure of the diazonium mechanism to account for all of the experimental facts. Details of their elegant experimental elucidation of the essential features of the second reaction course will be found in their paper.[3] Under the conditions of the best preparative procedure that was developed, it appears that no more than about 10% of the dinitrophenol is formed through benzenediazonium nitrate.[20] Phenylmercuric nitrate and nitrosobenzene are, however, intermediates common to both of the major routes to dinitrophenol.

In connection with the investigation of the mechanism of the oxynitration of benzene, a num-

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[18] (a) In the derivation of equation 1 the assumption is made that every molecule of diazonium salt is eventually converted into nitrophenol; the number of moles of nitrogen formed is therefore equal to the number of moles of dinitrophenol produced. Since the oxidation-reduction reactions are assumed to take place with complete efficiency, all the oxidized organic material is assumed to form carbon dioxide; (b) in the derivation of equation 2 the assumption is made that the material suffering destructive oxidation is either capable of generating one mole equivalent of nitrogen (*e. g.*, benzenediazonium nitrate), or has already liberated one molecular equivalent of nitrogen (*e. g.*, phenol formed through the diazonium sequence); in this case the number of moles of nitrogen produced is equal to the total number of moles of benzene reacting.

[19] Downing and Wright, Report on "The Direct Conversion of Benzene to Picric Acid," University of Toronto, May, 1942.

[20] The alternative path from nitrosobenzene to dinitrophenol discovered by Westheimer, Segel and Schramm does not require the formation of nitrogen gas along with the phenolic product. In some of our later preparative oxynitration runs, complete nitrogen balances showed that a maximum of approximately one mole of nitrogen is formed under the most favorable operating conditions during the formation of ten moles of dinitrophenol, and this may be interpreted as being a measure of the relative extent to which dinitrophenol is formed by the diazonium sequence. Data on these material balances will be published later.

ber of experiments were made to determine how various other possible intermediates or by-products behave under typical reaction conditions. For example, it was determined that a solution of benzenediazonium nitrate is converted into 2,4-dinitrophenol in yields of 61 to 67%. Phenol itself gave yields of 65–70% of dinitrophenol, and dark red by-products were always formed.

In view of the evidence that polymercuration occurs readily in dilute aqueous nitric acid, the fate of one dimercurated benzene derivative, *m*-diacetoxymercuribenzene, in nitric acid was investigated. A low yield of 2,4-dinitrophenol was obtained, but approximately 60% of the starting material could not be accounted for among the recognizable products. Subsequent to this experiment the kinetic measurements of Westheimer, Segel and Schramm showed that the steady-state concentration of phenylmercuric nitrate is quite low under optimum preparative conditions of oxynitration and that polymercuration probably occurs to a negligible extent. Polymercuration becomes significant only in dilute nitric acid or in the presence of agents which destroy nitrogen oxides.

The behavior of *p*-nitrobenzenediazonium nitrate under oxynitrating conditions was studied in view of the rather remote possibility that nitrophenylmercuric salts are formed in the reaction of benzene. The *p*-nitrodiazonium salt is very much more stable toward hydrolysis than the benzene analog, as has been shown by Cain and Nicoll.[21] The compound is converted into 2,4-dinitrophenol under oxynitrating conditions, but much more slowly than benzenediazonium nitrate.

Acknowledgment.—Reports of an investigation of the oxynitration of benzene to picric acid carried out at the University of Toronto under the direction of Professor George F. Wright between 1940 and 1942 were available to us and afforded much valuable information. Reports were exchanged frequently with the other contract groups under the N.D.R.C. We gratefully acknowledge the help which we received from these sources and from conferences with the other groups. We are greatly indebted to Professor E. C. Wagner of This Department, who followed the course of the investigation closely and contributed many valuable suggestions. We wish also to thank Dr. Ralph Connor, Chief of Section 8.2 of the N.D.R.C. and later Chief of Division 8, for his advice and encouragement.

Experimental

Isolation of Basic Phenylmercuric Nitrate from an Oxynitration Mixture.—Benzene (0.2 mole) was stirred with a solution of 0.2 mole of mercuric nitrate in 200 ml. of 35% nitric acid for seventy-five minutes at 62°. The mixture was cooled and diluted with water, causing the precipitation of 5.4 g. (8.6%) of basic phenylmercuric nitrate, m. p. 182–183° (reported m. p. 176–186°[13]; 187–190°[7]).

Oxynitration of Phenylmercuric Salts.—Powdered phenylmercuric acetate (56 g., 0.167 mole) was added to 450 ml. of 54.5% nitric acid contained in a large beaker. The mixture was vigorously stirred and the temperature maintained at 45°. The addition of the mercury compound was made in small increments at intervals of two minutes over a period of six hours. After a brief period of stirring following addition of all of the phenylmercuric acetate, the mixture was diluted with 450 ml. of cold water, chilled for several hours, and 17.7 g. of crystalline 2,4-dinitrophenol, m. p. 105–110°, was removed by filtration. Two further crops of dinitrophenol were obtained by extraction of the filtrate with benzene, extraction of the benzene solution with aqueous sodium hydroxide, and precipitation of the nitrophenol by acidification, giving a total yield of 70.4%. A neutral fraction amounting to 0.7 g. was obtained from the washed benzene solution by distillation. Only a trace of this material was nitrobenzene; the remainder resembled the dinitrobenzene fractions (predominantly *p*-dinitrobenzene) obtained as by-products of the oxynitration of benzene.

In a similar experiment in which the same proportions of reactants were used but the phenylmercuric acetate was added in 3-g. portions over a period of one and one-half hours (total reaction time, two hours), the yield of dinitrophenol fell to 55%, with a trace of nitrobenzene and about 0.77 g. of crude dinitrobenzene in addition to several grams of dark red by-products.

In a third experiment like the above except that the entire 56 g. of phenylmercuric acetate was added in one portion there resulted a spontaneous rise in temperature which was difficult to control. Only 20.8% of dark, impure 2,4-dinitrophenol was isolated, with 0.2 g. of nitrobenzene and 0.5 g. of crude *p*-dinitrobenzene. Most of the starting material was accounted for as dark, benzene-insoluble by-products.

Mercuration of Benzene in Dilute Nitric Acid.—A number of experiments were made in different concentrations of nitric acid. The following was typical of the conditions which seemed to give a maximum weight of mercurated material with only a small amount of nitrophenolic product formed simultaneously. A solution of mercuric nitrate in nitric acid was prepared by dissolving 38.7 g. of red mercuric oxide in a solution of 33.5 ml. of 70% nitric acid in 175 ml. of water (equivalent to 0.177 mole of mercuric nitrate in 207 g. of 5.3% nitric acid). Benzene (7.6 ml., 6.7 g., 0.086 mole) was added and the mixture was stirred and refluxed for three and one-half hours (disappearance of the benzene phase). The reaction mixture was chilled to 5° and a pale tan solid product was removed by filtration; yield 34.1 g. The solution was fortified with 4 ml. of 70% nitric acid and 30 g. of mercuric oxide, and a second portion of 6.7 g. of benzene was agitated with the mixture at reflux temperature for three and one-half hours. When the solution was chilled to 5°, 39.2 g. of solid mercurated material was filtered. The solution was again fortified with 4.4 ml. of 70% nitric acid and 33.0 g. of mercuric oxide, treated with a third portion of 6.7 g. of benzene as before, and 44.2 g. of solid mercurated material was obtained.

Fifty grams of solid mercurated product prepared by a procedure similar to the above was cleaved with bromine in the following manner. The powdered solid was suspended in 700 ml. of water, and bromine was added with vigorous agitation until a permanent color was observed. Benzene was added toward the end of the reaction to take up the organic products which separated. The temperature did not exceed 30°. The benzene layer was separated and washed with water. Filtration and concentration of the aqueous portion yielded 54.4 g. (0.151 mole) of crystalline mercuric bromide. Distillation of the benzene solution under reduced pressure yielded fractions, on the basis of whose boiling ranges the composition of the mixture was estimated as follows: 9 g. of bromobenzene, 10 g. of dibromobenzenes, 2.3 g. of tribromobenzenes and a solid residue of 0.9 g. which appeared to consist of tetrabromobenzene. When chilled, the dibromobenzene fraction yielded a total of 1.57 g. of *p*-dibromobenzene in several

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[21] Cain and Nicoll, *J. Chem. Soc.*, **81**, 1412 (1902).

fractions, m. p. 83–84°. The tribromobenzene fraction, when chilled to −10°, yielded 0.15 g. of crystalline solid, m. p. 114–115°; recrystallization from 75% alcohol gave a product melting at 119–119.5° (reported for 1,3,5-tribromobenzene, m. p. 120°[22]). In another similar experiment, the small residue of solid remaining after removal of fractions boiling below 265° gave, upon recrystallization from alcohol, crystals m. p. 168–172° (reported for 1,2,4,5-tetrabromobenzene, m. p. 177–178°[23]).

The method of cleavage by bromine was tested with phenylmercuric acetate; 14.5 g. of the pure compound was treated as described above, yielding 5.6 g. (80%) of bromobenzene and 13.5 g. (84%) of mercuric bromide, with no evidence of the formation of polybrominated benzene derivatives. In a similar manner 4.2 g. of *m*-diacetoxymercuribenzene yielded 1.3 g. (78%) of *m*-dibromobenzene and 4.28 g. (84%) of mercuric bromide.

A number of experiments were made to determine the yields of nitrophenols when the mixture of polymercurated benzene derivatives was added to nitric acid under oxynitrating conditions. The yields of 2,4-dinitrophenol seldom exceeded 30% based upon the over-all conversion from benzene, and considerable amounts of dark red tarry by-products were formed. *p*-Dinitrobenzene was identified among the reaction products.

Oxynitration of Nitrosobenzene.—A solution of 80 ml. of 30% nitric acid was stirred at 30° while a stream of nitric oxide was passed through continuously. To this reaction mixture 10.7 g. (0.10 mole) of finely powdered solid nitrosobenzene was added gradually during the course of one hour. The mixture was stirred for another fifteen minutes at 30°, then 67 ml. of 70% nitric acid was slowly added with stirring to increase the concentration of acid to approximately 50% by weight. The temperature rose rapidly to 50–55° and the mixture was stirred at this temperature for two hours. When the solution was chilled, crystalline 2,4-dinitrophenol separated and was removed by filtration; yield 9.7 g. (52.7%); m. p. 104–109°. Recrystallization from water yielded yellow plates, m. p. 109–112°.

Effect of Added Nitrogen Oxides upon the Yields in Oxynitration.—A number of batch oxynitration runs were made with variations of the standard procedure involving the vigorous agitation of benzene with a large excess of 50–55% nitric acid containing 0.2 to 0.5 *M* mercuric nitrate at temperatures in the neighborhood of 50°.[24,25] The yields of 2,4-dinitrophenol and picric acid in the best runs were in the range of 63 to 73% (without allowance for 5–10% of benzene swept from the reaction mixture by entrainment in the fume). In a series of parallel experiments, nitrogen oxides were generated externally in various ways and introduced into the otherwise conventional reaction mixtures: (1) nitrogen trioxide prepared by the action of concentrated nitric acid upon dry arsenious oxide[26]; (2) nitric oxide prepared by the action of sulfuric acid upon sodium nitrite solution.[27] In other runs nitrogen oxides were generated within the reaction mixture by several procedures: (1) intermittent addition of solid sodium nitrite or aqueous sodium nitrite alternated with extra fortifying nitric acid; (2) addition of hydroquinone with extra fortifying nitric acid. In still other runs basic phenylmercuric nitrate was added with agitation to nitric acid as described above while sodium nitrite solution was simultaneously introduced. In all of these modifications in which extra oxides of nitrogen were provided, lower yields of dinitrophenol were obtained than in corresponding procedures in which the only nitrogen oxides present were those resulting from the oxynitration reaction itself. In most cases the yields were only one-half or less the normal expected values, and the nitrophenols were contaminated with red by-products which were difficult to remove. The introduction of nitrogen oxides had the further disadvantages of increasing the proportion of benzene lost by entrainment in the fume and of accelerating the depletion of the nitric acid.

Nitrophenols from Benzenediazonium Nitrate.—A solution of 18.6 g. (0.20 mole) of aniline in 75 ml. of ice-cold 50% nitric acid was diazotized by means of a solution of sodium nitrite in 25 ml. of cold water. The solution of diazonium salt was dropped from a chilled dropping funnel into 600 ml. of vigorously stirred 50% nitric acid at 50°. The acid strength was held approximately constant during the three-hour addition period by fortification with 98% nitric acid. A yield of 15.1 g. of crystalline 2,4-dinitrophenol was filtered from the reaction mixture after thorough cooling, and an additional 9.5 g. of a mixture of 2,4-dinitrophenol and picric acid was isolated by extraction of the filtrate with benzene. The proportion of picric acid in the second crop was not determined; the total yield therefore was between the limits of 61.6 and 66.7%, depending upon the proportion of picric acid in the second crop.

Nitration of Phenol under Typical Oxynitrating Conditions.—A solution of 18.8 g. (0.2 mole) of phenol in 35 ml. of water was introduced from a heated dropping funnel beneath the surface of 600 ml. of vigorously stirred 50% nitric acid at 50°; the addition time was three hours and stirring was continued for another hour. The mixture was cooled to 0° and 19.5 g. of 2,4-dinitrophenol was filtered. Extraction of the filtrate with benzene yielded 6.4 g. of a mixture of 2,4-dinitrophenol and picric acid. On the assumption that the second crop contained approximately equal parts of the two products (as shown by analysis in another run under similar conditions), then the total yield of nitrophenolic material was 68%.

Reaction of *m*-Diacetoxymercuribenzene with Nitric Acid.—Mercuric acetate (45 g.) and 21 g. of potassium *m*-benzenedisulfinate were heated together in 600 ml. of glacial acetic acid for two hours. The clear filtrate from the mixture was freed of solvent by distillation under reduced pressure and the residue was washed with dilute nitric acid. The dried solid product weighed 30.1 g. A portion of this material (17.8 g.) was suspended in 25 ml. of water and 63 ml. of 70% nitric acid was added with stirring. The temperature rose to 48° and the mixture darkened. It was stirred at 45° for one and one-half hours, then was diluted with three volumes of water and extracted with benzene. From the clarified benzene extracts was isolated, in several fractions, 1.75 g. of material melting at 105–109°, not depressed by mixture with 2,4-dinitrophenol. Recrystallization from 50% alcohol raised the melting point slightly, and the recrystallized material showed no depression when mixed with pure 2,4-dinitrophenol. No other identifiable material was isolated from the mixture.

Behavior of *p*-Nitrobenzenediazonium Nitrate under Oxynitrating Conditions.—*p*-Nitroaniline (27.6 g., 0.20 mole) was diazotized in 75 ml. of 50% nitric acid at 0–5° by addition of a cold solution of 15 g. of sodium nitrite in 25 ml. of water. To the resulting solution was slowly added 65 ml. of 98% nitric acid. A small amount of nitrogen oxide fume appeared during the last step. The solution was stirred at 50° for one and one-half hours, then chilled for about twelve hours. No crystals separated from the deep yellow solution, and a small sample of the solution still gave a test for diazonium salt with β-naphthol

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(22) Ssabanejew, *J. Russ. Phys. Chem. Soc.*, **17**, 176 (1885).

(23) Zelinsky, *Ber.*, **34**, 2803 (1901).

(24) Manganous nitrate and/or aluminum nitrate were sometimes added. Although Davis, *et al.* (ref. 25), reported that manganous and aluminum salts have no promoter action in oxynitration, other investigators have recommended their use. We did not observe any significant effect upon the yields attributable to aluminum nitrate. The possibility is not excluded that aluminum salts may have catalytic action under other experimental conditions. G. F. Wright (private communication) has observed such effects in his process for picric acid. Manganous nitrate did not appear to improve the yields of oxynitration products, but it does catalyze the oxidation of the by-product, oxalic acid, to carbon dioxide, thus aiding in preventing its excessive accumulation in the solution. Manganous nitrate was also found to catalyze the direct nitration of mono- and dinitrophenols.

(25) Davis, Worrall, Drake, Helmkamp and Young, THIS JOURNAL, **43**, 549 (1921).

(26) "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., Coll. Vol. I, 2nd ed., 1941, p. 266.

(27) Noyes, THIS JOURNAL, **47**, 2170 (1925).

solution. Extraction with benzene gave 3.2 g. (8.7%) of light yellow crystals of pure 2,4-dinitrophenol, m. p. 113–114°.

Basic Phenylmercuric Nitrate from Phenylmercuric Acetate.—One hundred grams of powdered phenylmercuric acetate was added gradually to a solution of 125 ml. of concentrated ammonium hydroxide (28%) in 400 ml. of water heated on a steam cone. An additional 20 ml. of concentrated ammonia was added, after which most of the solid had dissolved. The solution was heated to boiling and filtered directly into 75 ml. of vigorously stirred 70% nitric acid. An additional 5 ml. of 70% nitric acid was introduced into the mixture, which was then boiled for one minute, cooled to 5°, and filtered. The solid, after being washed with ice water and dried, consisted of 73.3 g. (77.5%) of white basic phenylmercuric nitrate, m. p. 181–182° (dec.).

Summary

Studies of some of the intermediate stages in the oxynitration of benzene are described. Basic phenylmercuric nitrate was isolated from an oxynitration reaction mixture. Phenylmercuric salts were shown to react with nitric acid to produce 2,4-dinitrophenol. The mercuration of benzene in dilute nitric acid was studied. Nitrosobenzene was oxynitrated without the use of mercuric nitrate as a catalyst. The stoichiometric consequences of Darzens' proposed mechanism for oxynitration were investigated. The fate of some other possible intermediates was studied under typical oxynitration conditions. A convenient procedure was developed for the conversion of phenylmercuric acetate into basic phenylmercuric nitrate.

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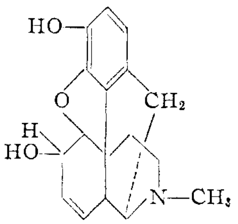
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Angular Aryl Group. 10-Phenyldecahydroquinoline and 9-Phenyldecalin

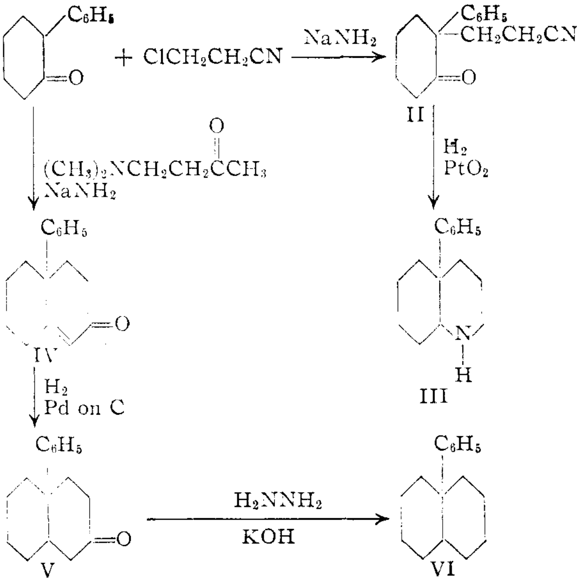
BY VIRGIL BOEKELHEIDE[1]

Although considerable research has been done on compounds with fused rings having a methyl group at the angular position, relatively few compounds have been synthesized having an angular group other than methyl.[2] It might be thought that there is insufficient free space at the angular position for a large group. Yet this is not borne out by the experimental work that has been done. Thus Allen and VanAllan were able to establish that treatment of methylanhydroacetonebenzil with acid yielded a compound having an angular phenyl group.[3] Also Allen, Bell, Clark and Jones have reported some reduced naphthoquinones having an angular phenyl group.[4] The angular aryl group is important in regard to the structures which have been proposed for morphine[5] and for strychnine.[6] Thus the Gulland and Robinson structure for morphine, as shown below in formula I, may be regarded as an octahydroisoquinoline derivative having an angular aryl group. The work to be described was carried out for the purpose of preparing some model compounds of relatively simple structure which would have an angular aryl group.



I

The synthesis of 10-phenyldecahydroquinoline was readily accomplished in fair yield by the scheme shown below. The reaction of 2-phenylcyclohexanone with β-chloropropionitrile in the presence of sodium amide gave 2-(β-cyanoethyl)-2-phenylcyclohexanone, II. The location of the cyanoethyl group was established by the reaction of II with benzaldehyde. The formation of the



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[2] Examples of angular groups other than methyl that have been reported in the literature include the following: ethyl (Ghosh and Robinson, *J. Chem. Soc.*, 506 (1944)), allyl, (Grewe, *Ber.*, **76**, 1072 (1943)), dichloromethyl (Woodward, THIS JOURNAL, **62**, 1208 (1940)), and carbethoxyl (Fieser and Holmes, *ibid.*, **60**, 2548(1938)).

[3] C. F. H. Allen and J. VanAllan, THIS JOURNAL, **64**, 1260 (1942); *J. Org. Chem.*, **10**, 333 (1945).

[4] Allen, Bell, Clark and Jones, THIS JOURNAL, **66**, 1617 (1944).

[5] Gulland and Robinson, *Mem. Proc. Manchester Lit. & Phil. Soc.*, **69**, 79 (1925).

[6] Briggs, Openshaw, and Robinson, *J. Chem. Soc.*, 903 (1946); Prelog and Metzler, *Helv. Chim. Acta*, **29**, 1163 (1946).