added 0.5 g. (0.020 mole) of osmium tetroxide in 25 ml. of ether. Since some of the olefin had a tendency to precipitate with the osmium tetroxide complex, best results were obtained by mixing the hot solutions. In the most successful experiment, 1.0 g. (80%) of the complex was obtained which was converted to the glycol as described for the oxidation of *trans*-I to give 0.24 g. (46% yield) of glycol (*threo*-VII), m.p. 128–129°.

Reaction of *cis*-*p*-Methoxy-*p*'-methylstilbene (*cis*-V) with Perbenzoic Acid.—*cis*-V (2.1 g., 0.010 mole) was treated with 1.6 g. (0.012 mole) of perbenzoic acid in 80 ml. of chloroform at 0° for 48 hours, after which the solution was washed with dilute sodium carbonate solution, and the solvent evaporated. The oily product crystallized from benzene–petroleum ether solution, and, after recrystallization, amounted to 1.4 g. (0.004 mole, 40%) of hydroxy benzoate, *erythro*-VII, m.p. 139–142°. Two additional recrystallizations raised the m.p. to 144°.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.2; H, 6.1. Found: C, 76.3; H. 5.9.

The hydroxy benzoate (0.65 g.) was hydrolyzed by treatment under reflux with 80 ml. of 1.7 *M* potassium hydroxide to which had been added 20 ml. of methanol. On cooling of the reaction mixture, the glycol (*erythro*-VII) crystallized and was recrystallized from benzene–ligroin. When purified it amounted to 0.27 g. (58%) and had m.p. 134–135° both alone and when admixed with the product, m.p. 134–135°, obtained from the osmium tetroxide oxidation described below.

Reaction of *cis*-V with Osmium Tetroxide.—The oxidation of *cis*-V (0.44 g., 0.0020 mole) was carried out by the method employed for *cis*-I to give 0.32 g. (0.0012 mole, 63% yield) of glycol (*erythro*-VII), m.p. 134–135°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.4; H, 7.0. Found: C, 74.3; H, 6.8.

***trans*-*p*-Methoxy-*p*'-methylstilbene Oxide (*trans*-VIII).**—The conversion of the *trans*-olefin (*trans*-V) to the epoxide was carried out by way of the dibromide in a method completely analogous to that employed with *trans*-I. The epoxide, m.p. 78–82°, was obtained from dibromide in 57% yield and when recrystallized had m.p. 84–85°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 79.8; H, 7.0.

Reaction of the Epoxide (*trans*-VIII) with Benzoic Acid.—The epoxide (0.30 g.) was treated with benzoic acid (0.30 g.) in 10 ml. of chloroform for 1 hour at room temperature after which 30 ml. more of chloroform was added, the solution was washed with aqueous sodium carbonate, dried and evaporated to 5-ml. volume. On dilution with 20 ml. of petroleum ether the hydroxy benzoate (*threo*-VI) crystallized and was collected by filtration and washed with petroleum ether to give 0.29 g. (64%) of crystals, m.p. 139–140°. The m.p. of a mixture with a sample of *threo*-VI obtained above showed no depression.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SANITARY CHEMISTRY BRANCH, CHEMICAL CORPS MEDICAL LABORATORIES]

The Chlorine-catalyzed Hydrolysis of Isopropyl Methylphosphonofluoridate (Sarin) in Aqueous Solution

BY JOSEPH EPSTEIN, VIRGINIA E. BAUER, MELVIN SAXE AND MARY M. DEMEK

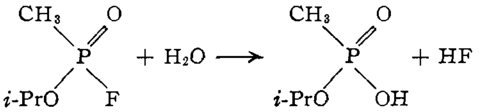
RECEIVED JANUARY 14, 1956

The decomposition of isopropyl methylphosphonofluoridate (Sarin) in aqueous solutions of chlorine has been studied in the *p*H region 5 to 9. Sarin decomposes, as in a simple hydrolysis, with the formation of two acids. The hydrolysis is catalyzed by hypochlorite ion, and the rate is proportional to the first powers of hypochlorite ion and Sarin. The bimolecular rate constant has a value of approximately 600 l. mole^{-1} min.$^{-1}$ at 25°. A mechanism for the reaction consistent with observations is proposed. An explanation for the high nucleophilicity of the hypochlorite ion toward Sarin is advanced.

Introduction

In connection with drinking water purification studies carried out in these laboratories it was of interest to study the behavior of the nerve gas Sarin (isopropyl methylphosphonofluoridate) in dilute aqueous solution containing an approximately equivalent concentration of active chlorine compounds.

In slightly acid and slightly alkaline solutions of chlorine, Sarin decomposes with the formation of two moles of acid as in a simple hydrolysis, but at



a much more rapid rate than is observed for a spontaneous hydrolysis.[1]

The decomposition of Sarin at constant *p*H, even in solutions containing approximately equivalent concentrations of Sarin and chlorine, followed by both the disappearance of Sarin and the appearance of acid, is kinetically of first order (Fig. 1). Moreover, the concentration of the active chlorine compound remains constant during the course of the hydrolysis.

Analysis of rate data at constant *p*H (Table I) by the differential method[2] indicates that the reaction is bimolecular, the rate of decomposition of Sarin being proportional to the first powers of the Sarin and chlorine concentrations.

TABLE I

RATE DATA OF SARIN DECOMPOSITION[a] IN AQUEOUS CHLORINE SOLUTION[b]

Sarin, $M \times 10^4$	Chlorine, $M \times 10^3$	$k_{obs.} \times 10^2$, min.$^{-1}$
2.14	2.12	4.6
4.28	2.12	4.0
8.56	2.12	4.6
2.14	0.71	1.6
2.14	2.82	6.1

[a] All experiments performed at constant *p*H 6.0 and temperature 24.0 ± 0.5°. [b] High test hypochlorite (HTH) manufactured by Mathieson Chemical Corp. used as the source of chlorine.

---

[1] In fact, for many of the experiments described herein, the spontaneous hydrolysis rate was negligible (*i.e.*, <1%), as compared to the hydrolysis rate of Sarin in the presence of chlorine. The spontaneous hydrolysis rate constant of Sarin determined at 25° at *p*H 5 and 6 is approximately 6×10^{-5} min.$^{-1}$, at *p*H 7, 2×10^{-4} min.$^{-1}$, at *p*H 8, 2×10^{-3} min.$^{-1}$ and *p*H 9, 2×10^{-2} min.$^{-1}$.

[2] S. Glasstone, "Textbook of Physical Chemistry," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1067.

Over a range of *p*H from 5 to 9, however, a second-order rate constant, k_2, calculated by dividing the observed first-order constant corrected for the spontaneous hydrolysis ($k_{obs} - k_s$) by the total chlorine concentration varies with *p*H and a true bimolecular constant, k_2, is obtained if hypochlorite ion concentration is substituted for total chlorine concentration (Table II).

TABLE II

DECOMPOSITION OF SARIN (2×10^{-4} *M*) IN AQUEOUS CHLORINE SOLUTIONS[a] AT VARIOUS *p*H's, $T = 24.0 \pm 0.5°$

*p*H	Chlorine concn., $M \times 10^3$	$(k_{obs} - ks) \times 10^2$, min.$^{-1}$	$k_2 \times 10^{-2}$, l. mole^{-1} min.$^{-1}$	$k_2 \times 10^{-2}$, l. mole^{-1} min.$^{-1}$
5.0	2.82	0.72	0.026	6.4
6.0	0.705	1.63	.23	6.0
	2.12	4.59	.22	5.6
	2.82	6.08	.22	5.6
7.0	0.265	3.61	1.4	4.8
	.354	5.46	1.5	5.4
8.0	.044	2.06	4.7	5.9
	.132	5.82	4.4	5.3
	.176	8.19	4.6	5.6
9.0	0.044	2.49	5.7	5.8
	0.062	3.58	5.8	5.9

[a] High test hypochlorite (HTH) used as source of chlorine.

The hypochlorite ion concentration at any *p*H was calculated from the equation

$$[\mathrm{OCl^-}] = \frac{K_A[\mathrm{Cl_2}]}{[\mathrm{H^+}] + K_A}$$

where $[\mathrm{Cl_2}]$ is the total molar chlorine concentration and K_A is the acid dissociation constant[3] of hypochlorous acid at 25° chosen for this work as 4×10^{-8}.

The bimolecular rate constant, k_2, was calculated from the equation

$$k_2 = \frac{(k_{obs} - k_s)([\mathrm{H^+}] + K_A)}{K_A[\mathrm{Cl_2}]}$$

At $pH << 6$, and where $k_{obs} >> k_s$, this equation reduces to

$$k_2 = \frac{k_{obs}[\mathrm{H^+}]}{K_A[\mathrm{Cl_2}]}$$

Further studies, involving changes of the cation associated with hypochlorite ion, such as sodium or calcium, and kinetic measurements of the rate of disappearance of Sarin in the presence of hypochlorous acid (free of chloride ion) suggest that only the hypochlorite ion is involved in the reaction (Table III).

TABLE III

EFFECT OF SOURCE OF HYPOCHLORITE ON RATE

Source of hypochlorite	Other ions in soln.	Av. $k_2 \times 10^{-2}$, l. mole^{-1} min.$^{-1}$
HTH	$\mathrm{Ca^{++}}$, $\mathrm{Na^+}$, $\mathrm{Cl^-}$	5.6
NaOCl	$\mathrm{Na^+}$, $\mathrm{Cl^-}$	6.0
HOCl	$\mathrm{Na^+}$, $\mathrm{NO_3^-}$	6.2

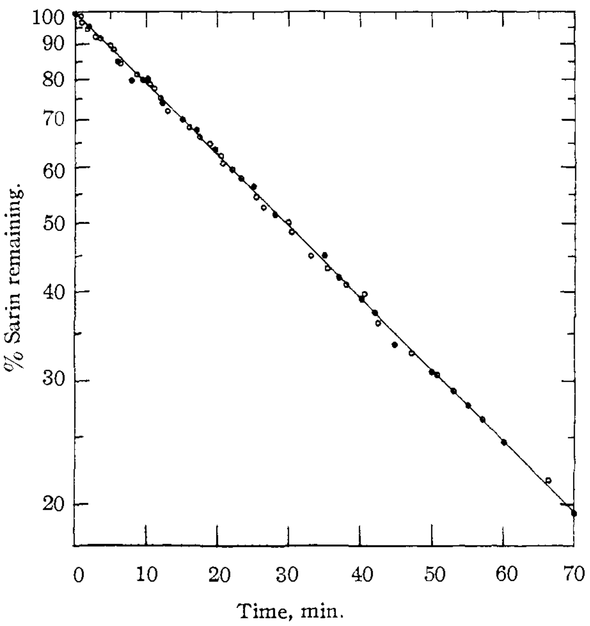


Fig. 1.—Hydrolysis rate of Sarin at *p*H 6, $T = 24 \pm 0.5°$, $[\mathrm{OCl}] = 1.13 \times 10^{-3} M$, $[\mathrm{Sarin}] = 4.28 \times 10^{-4} M$: ●, colorimetric test for unreacted Sarin; ○, Sarin by acid production.

Chloramines apparently do not possess the effectiveness of the hypochlorite ion for accelerating the hydrolysis of Sarin. The speed of hydrolysis of Sarin in a solution 3×10^{-3} *M* with respect to Chloramine T was, within the limits of experimental error, the same as the rate in the absence of the chloramine. Moreover, the effect of the hypochlorite salt is completely inhibited if the hypochlorite salt is introduced into a solution containing Sarin and an ammonium salt. It has been shown that hypochlorite is rapidly converted to chloramine by ammonium ions.[5]

The observations reported herein suggest that the hydrolysis of Sarin is catalyzed by hypochlorite ion. In addition to the fact that the active chlorine concentration by titration remains constant,[6] other arguments may be advanced to illustrate the catalytic nature of the reaction. For example, upon complete hydrolysis, two moles of acid is produced per mole of reacted Sarin. More than two moles of acid might be expected if the reaction involved a destruction of hypochlorous acid, since hydrochloric acid is usually produced under these conditions. Also the hydrolysis of Sarin at constant *p*H in a solution containing an approximately equivalent concentration of chlorine was allowed to proceed until more than 80% of the Sarin had been destroyed. The rate was calculated from the uptake of sodium hydroxide solution. Fresh Sarin was then added and the reaction rate was again determined from the volume of alkali needed to maintain a constant *p*H. The rate constants of the

---

(3) The value of the constant chosen is an average of several reported in the literature.[4] The absolute value of k_2, since it depends upon the value of K_A must be considered only approximate. The constancy of the k_2 values of *p*H are not seriously affected by the uncertainty in the value of K_A.

(4) See, *e.g.*, M. C. Sneed, J. L. Maynard and R. C. Brasted, "Comprehensive Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., Vol. III, 1954, p. 153.

(5) I. Weil and J. C. Morris, THIS JOURNAL, **71**, 1664 (1949).

(6) That the chlorine concentration remains constant may also be deduced from a consideration of the observed order of reaction and the true order. In bimolecular reactions, in which the reactants are present in approximately equal concentrations, first-order kinetics will be observed only if one of the reactants remains constant.

two experiments were, within the limits of experimental error, identical.

The effect of temperature on the reaction rate is shown in Table IV.

TABLE IV

EFFECT OF TEMPERATURE

Temp., °C.	$k_{obs} \times 10^2$, min.^{1}	$1/T \times 10^3$
3.5	0.826	3.60
23.5	3.07	3.37
34.0	5.78	3.26

The slope of the straight line obtained by plotting the reciprocal of the absolute temperature against the logarithm of the first-order rate constants was used in the Arrhenius equation $d \ln k/dT = E/RT$ to calculate the energy of activation, E. The value of E calculated in this manner was 11.4 kcal.

Experimental

Apparatus.—A Precision Scientific Company constant temperature bath maintained a jacketed cylindrical reaction vessel at ±0.5°. Constant *p*H was maintained by the use of a Beckman Automatic Titrator set to a desired *p*H or by the addition of sodium hydroxide solution from a graduated micropipet. Colorimetric readings were made on a Klett-Summerson photoelectric colorimeter with a no. 42 filter and *p*H was measured with a Beckman Model G *p*H meter.

Materials.—Sarin, purity >95%, was obtained from the Chemical Research Division of the Chemical Warfare Laboratories. High test hypochlorite, a product of Mathieson Chemical Corporation, contained calcium hypochlorite, not less than 70% and inert ingredients not more than 30%. Solutions of sodium hypochlorite were prepared in these laboratories by standard methods.[7] Hypochlorous acid, free of chloride ion, was prepared by the method of Jakowkin.[8] Reagents used for the colorimetric analysis of Sarin have been previously described.[9]

Procedure.—In each experiment 250 ml. each of freshly prepared Sarin and the hypochlorite solutions, adjusted to the desired *p*H, was added simultaneously to the reaction vessel. The *p*H was maintained constant by automatic (Beckman Titrator) or manual addition of 0.2 *N* sodium hydroxide solution. From time to time, aliquots of the reaction mixture were analyzed colorimetrically,[10] for the concentration of unreacted Sarin.

Plots of the logarithm of $(a - x)/a$ against time were made, where a is the original concentration of the Sarin and $(a - x)$ is the concentration of Sarin at time t. The observed first-order constant (k_{obs}) was determined from the graphs using the relationship $k_{obs} = 0.693/t_{1/2}$ where $t_{1/2}$ is the half-life of the Sarin.

As checks, the rate constants were calculated from base uptake rates in several experiments. The logarithm of the fraction $(V_\infty - V_t)/V_\infty$ where V_∞ is the volume of base required if the reaction were complete (determined by potentiometric back titration of an aliquot to the Sarin solution containing an excess of standard alkali) and V_t is the uptake of base solution at time t, was plotted against time. In those experiments where aliquots of the reaction mixture were extracted for colorimetric analysis, adjustments were made in the V_∞ values to compensate for the loss of Sarin. The rate constants determined by the two methods were in excellent agreement (see *e.g.* Fig. 1).

The spontaneous hydrolysis rate constants for Sarin in the absence of chlorine or active chlorine containing compounds for each experimental condition were determined to allow calculations of the k_s values. The observed first-order (k_{obs}) less the first-order constant for spontaneous hydrolysis (k_s) gives the constant due to the chlorine reaction with Sarin.

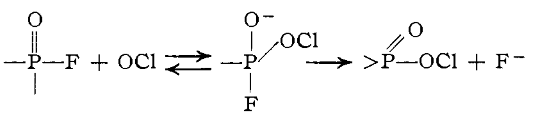
Aliquots of the reaction mixture containing approximately 0.4 mg. of Sarin were treated with 2 ml. of an aqueous solution 5% with respect to Calgon (a commercial preparation of sodium hexametaphosphate) and 0.4% with respect to hydrogen peroxide for 30 seconds in a 100-ml. volumetric flask.[11] Then 10 ml. of a buffer-indicator mixture (composed of 200 ml. of 0.05 *M* phosphate buffer, *p*H 8.8; 200 ml. of aldehyde-free acetone and 100 ml. 1% aqueous *o*-tolidine dihydrochloride), followed by 4 ml. of a freshly prepared aqueous solution of sodium perborate, $1\%_1$ was added to the flask. The solutions were diluted to 100 ml., mixed well and read after 30 minutes in a photoelectric colorimeter.

The active chlorine concentration was determined by titration according to well established procedures.[12]

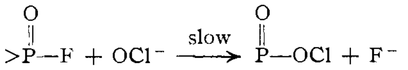
The rate of hydrolysis of Sarin in the presence of chloramines was determined from the rate of alkali uptake only.

Discussion

A tentative reaction mechanism consistent with (a) the absence of hypochlorite consumption during the course of an experiment, (b) the first-order dependence on Sarin and hypochlorite ion concentration[13] and (c) the non-dependence of the reaction rate upon anions such as chloride is


(1)

or, by direct displacement


$$>\overset{\overset{\displaystyle O}{\|}}{P}\text{—F} + OCl^- \xrightarrow{\text{slow}} \overset{\overset{\displaystyle O}{\|}}{P}\text{—OCl} + F^- \quad (1a)$$


$$>\overset{\overset{\displaystyle O}{\|}}{P}\text{—OCl} + H_2O \xrightarrow{\text{fast}} >\overset{\overset{\displaystyle O}{\|}}{P}\text{—OH} + HOCl \quad (2)$$

where steps 1 or 1a contain the rate-controlling step. It is believed that step 2 proceeds *via* a cleavage of the O to Cl bond.[14]

The peculiar effectiveness of the hypochlorite ion as an hydrolysis catalyst is of interest. Ed-

---

[7] *E.g.*, "Standard Methods for the Examination of Water and Sewage," Eighth Edition, Seventh Printing, Lancaster Press, Inc., Lancaster, Pa., 1943, p. 144.

[8] A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[9] J. Epstein, D. H. Rosenblatt and M. M. Demek, THIS JOURNAL, **78**, 341 (1956).

[10] J. Epstein and V. E. Bauer, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Feb. 27-March 2, 1956-

[11] The purpose of this treatment is to destroy the hypochlorite which would interfere with the colorimetric test. For the highest concentrations of chlorine used in these tests, *viz.*, 2.83×10^{-3} *M*, it was necessary to add an additional 2 ml. of 0.4% hydrogen peroxide solution. Calgon was necessary only when the high test hypochlorite (HTH) was used as the source of hypochlorite. Its function was to complex (and thus prevent precipitation of) the calcium ion at the alkaline *p*H of the test.

[12] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 307.

[13] Since the hypochlorite ion concentration is related to the products of the concentrations of free hypochlorous acid and hydroxyl ion by a constant, one cannot, from the kinetic data, state that hypochlorite ion *must* be involved in the mechanism. In fact, for the formation of alkyl hypochlorites, Anbar and Dostrovsky[14] propose a mechanism involving hypochlorous acid and hydroxyl ion rather than hypochlorite ion. Their choice of the active participants is based upon the fact alkyl hypochlorites do not form in solutions with *p*H higher than ten. It appeared to us that Anbar and Dostrovsky's[14] findings are not inconsistent with the assumption that the hypochlorite ion *is* involved in the mechanism. Consider the equilibrium

$$ROH + OCl^- \rightleftarrows ROCl + OH^-$$

At *p*H ≥ 10 virtually all of the active chlorine in solution will be present as hypochlorite ion and the rate of production of the alkyl hypochlorite will be unaffected by further increases in alkalinity. On the other hand, increase of hydroxyl ion would increase the reverse reaction rate with the result that less of alkyl hypochlorite will be formed.

[14] The cleavage of the O to Cl bond has been shown to occur in the hydrolysis of alkyl hypochlorites by the use of O^{18}-labeled compounds by M. Anbar and M. J. Dostrovsky, *J. Chem. Soc.*, 1094 (1954).

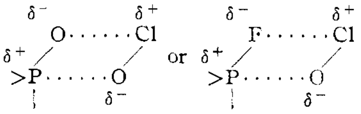
wards[15] has been able to correlate many rate data of the nucleophilic displacement type by assigning numerical values to nucleophiles based upon their electrode potentials (E_n) and basicities to protons (H). The values for hypochlorite ion, using Edwards' equations,[15] along with those of the hydroxide ion and the thiosulfate ion are shown below.

Ion	E_n	H
OH^-	1.65	17.48
$S_2O_3^=$	2.52	3.60
OCl^-	2.01	9.14

The relative importance of the two parameters will depend upon the compound under attack. For example, displacements on carbon compounds are very rapid with compounds of high E_n values, whereas the basicity factor appears to be more important in displacements on hydrogen.[15] It has been found in independent experiments that the thiosulfate ion, a material with a high E_n value and a powerful nucleophile toward carbon,[16] does not accelerate the hydrolysis rate of Sarin. It has also been established from studies of the hydrolysis of diisopropyl phosphorofluoridate[17] that the effectiveness of a nucleophile in this reaction was related to its basicity. Thus it might be conjectured that for displacements on phosphorus, the rate will be more correlatable with the nucleophile's ability to accept protons. Yet hydroxyl ion, which is more basic than hypochlorite ion by eight powers of ten, has a bimolecular rate constant (calculated from the data in footnote (1)) of only three to four times that of the hypochlorite ion. It would thus appear that the basicity alone of hypochlorite ion cannot be used to explain its activity.

It is proposed that the enhanced reactivity of the hypochlorite ion is due to a bifunctional attack,[18] the oxygen of the hypochlorite attacking the phosphorus atom and the positive chlorine attacking the phosphoryl oxygen (or the fluorine) thereby inducing polarization and aiding in displacement.

The transition state is depicted as



The effective van der Waals radii and the bond lengths[19] of the participating groups are such as to make such a postulation plausible, and spectral studies on various organic phosphorus compounds indicate the phosphoryl group is subject to polarization.[20]

---

[15] J. O. Edwards, THIS JOURNAL, **76**, 1540 (1954).

[16] P. D. Bartlett and G. Small, *ibid.*, **72**, 4867 (1950).

[17] M. Kilpatrick and M. L. Kilpatrick, *J. Phys. Colloid Chem.*, **53**, 1371 (1949).

[18] See *e.g.*, C. G. Swain and J. F. Brown, THIS JOURNAL, **74**, 2538 (1952); J. Epstein, D. H. Rosenblatt and M. M. Demek, *ibid.*, **78**, 341 (1956).

[19] L. Pauling, "Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1945, p. 164, 189.

[20] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, THIS JOURNAL, **76**, 5185 (1954); G. F. Svatos and J. Goldenson, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Feb. 27–March 2, 1956.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Displacements and Nuclear Substitutions on Hydroxypyrazines

BY GEORGE KARMAS[1] AND PAUL E. SPOERRI

RECEIVED MARCH 15, 1956

A variety of 2-hydroxypyrazines has been brominated and phenylated, and three have been nitrated. It has been found that halogens and nitro groups *ortho* to hydroxyl are easily displaced by acidic reagents, and such reactions afford convenient syntheses of dihalo- and dihydroxypyrazines.

I. Nitration.—In 1953, we reported that 2-hydroxy-5,6-diphenylpyrazine is readily nitrated in the 3-position under mild conditions and that 2-hydroxy-3,6-diphenylpyrazine undergoes random nitration under a variety of strongly acidic conditions.[2] Since then we have found that briefly boiling an acetic acid solution of equivalent amounts of nitric acid and the 3,6-diphenyl isomer leads to a 75% yield of the 2-hydroxy-5-nitro-3,6-diphenylpyrazine.

When one equivalent of nitric acid is added to a solution of 2-hydroxy-3-phenylpyrazine, the nitrate of this pyrazine soon crystallizes. This salt is stable in air but is hydrolyzed in water. Boiling in water does not effect nitration, but if the salt is briefly boiled in acetic acid, 2-hydroxy-3-phenyl-5-nitropyrazine is formed. Presumably, in hot acetic acid, dissociation of the nitrate is a relatively slow, temperature-dependent process which is followed by very rapid nitration of the nucleus.

The nitrates of the diphenylhydroxypyrazines, which are weaker bases, could not be isolated, and so it may not yet be assumed that they are intermediates as in the nitration of 2-hydroxy-3-phenylpyrazine.

Structures of the 5-nitropyrazines were proved by conversion to ethers which had alternatively been synthesized by independent methods to be described below and based in part on the elegant conversion of N-oxides to chloropyrazines as reported by Newbold and Spring.[3]

No conditions have been found for the nitration of alkylhydroxypyrazines. These reacted with nitric acid in hot acetic acid, but no pyrazinoid products could be isolated.

II. Bromination.—*para*-Substitution in 2-hydroxy-3,6-diphenylpyrazine and 2-hydroxy-3-(*sec*-

---

[1] Ortho Pharmaceutical Corporation, Raritan, New Jersey.

[2] G. Karmas and P. E. Spoerri, THIS JOURNAL, **75**, 5517 (1953).

[3] G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, 1183 (1947).