

brown within 5 min. After addition of 0.1 g. of fused potassium acetate, heating was continued with good stirring for 2 hr. The mixture was stirred at room temperature for an additional 12 hr. and poured into 250 ml. of anhydrous ether. The orange-yellow material (3.0 g.) which separated, was purified by solution in hot dimethylformamide and filtration of the solution into hot benzene. After cooling, addition of ether gave 1.3 g. of product, m.p. above 300°. The ultraviolet spectrum showed  $\lambda_{\max}$  270 m $\mu$  ( $\epsilon$  11,300) in dimethylformamide.

*Anal.* Calcd. for  $C_{19}H_{17}Cl_2N_5O_2S$ : C, 50.66; H, 3.77; N, 15.55. Found: C, 50.87; H, 3.97; N, 15.42.

*2,6-Dimethyl-4-hydroxythiazolo[2,3-f]purine (XV).* A mixture of 1.8 g. (0.01 mole) of VII, 1.2 g. (0.013 mole) of chloroacetone and 200 ml. of absolute ethanol was refluxed for 5 days. After 24 hr. an additional 1.2 g. of chloroacetone was added. The precipitate was filtered from the hot mixture and dissolved in cold dilute potassium hydroxide solution. After filtering from a small amount of insoluble material, acidification of the filtrate with acetic acid gave 1.75 g. of white crystalline material. After recrystallization by concentration of its solution in 500 ml. of ethanol to about half its volume, the substance formed fibrous crystals, m.p. above 300°. The ultraviolet spectrum showed  $\lambda_{\max}$  241 m $\mu$  ( $\epsilon$  20,300) and a shoulder at 272 m $\mu$  ( $\epsilon$  12,100) at pH 1;  $\lambda_{\max}$  242 m $\mu$  ( $\epsilon$  27,100) and  $\lambda_{\max}$  271 m $\mu$  ( $\epsilon$  12,600) at pH 11.

*Ethyl 6-hydroxy-2-methyl-8-purinylmercaptoacetate (XVI), R = CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>.* A mixture of 1.8 g. (0.01 mole) of VII, 5.0 g. of ethyl chloroacetate and 200 ml. of 95% ethanol was heated under reflux with stirring for 65 hr. The resulting clear solution was filtered from a small amount of impurities and concentrated to about 50 ml. on the steam bath. Dilution of the hot concentrate with hot water and cooling gave crystalline material. After purification by solution in methanol, dilution and distillation of the methanol, 0.5 g. of fine needles, m.p. 233–235° (dec.), was obtained.

When ethyl bromoacetate was substituted for ethyl chloro-

acetate, a clear solution (indicating complete reaction) was obtained after refluxing for 3 hr.

B. A mixture of 1.82 g. (0.01 mole) of VII, 2.0 g. (0.014 mole) of bromoacetic acid and 110 ml. of 95% ethanol was heated under reflux with stirring. After 16 hr., a clear brown solution resulted, from which 1.5 g. of XVI (R = CH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>) was isolated.

The other esters of 6-hydroxy-2-methylpurine-8-thioacetic acid were prepared by method B, using the appropriate alcohol as solvent. Melting points and analytical data are given in Table I. All the acetates showed characteristic infrared absorption peaks at 1160–1190 and 1720–1750 cm.<sup>-1</sup>

*6-Hydroxy-2-methyl-8-purinylmercaptoacet-p-fluoroanilide.* [XVI, R = CH<sub>2</sub>CONHC<sub>6</sub>H<sub>4</sub>F(*p*)]. A mixture of 2.4 g. (0.01 mole) of VIII, 10 ml. of benzene, and 10 ml. of *p*-fluoroaniline was heated under reflux with stirring, using a water separator, for 24 hr. The deep brown mixture was cooled, diluted with methanol and filtered to give 2.1 g. of nearly white solid, which did not melt at 300°. The solid was dissolved in one l. of boiling water, filtered and concentrated to about 250 ml. On cooling 1.1 g. of white solid, m.p. above 300°, separated.

*6-Hydroxy-2-methyl-8-purinylmercaptoacetylhydrazide.* (XVI, R = CH<sub>2</sub>CONHNH<sub>2</sub>). A solution of 1.0 g. of 95% hydrazine hydrate in 10 ml. of ethanol was added to a solution of 0.74 g. (0.0025 mole) of XVI (R = CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) in 20 ml. ethanol. The mixture was heated under reflux for about 1.5 hr. The mixture was refrigerated for 12 hr. and the white precipitate (0.6 g.) filtered. It was purified by solution in cold dilute potassium hydroxide and reprecipitation by acetic acid. The cream-colored solid did not melt until 300°.

*Acknowledgment.* We acknowledge the valuable assistance of James Hudson in the preparation of certain of the intermediates used in this work.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, PUREX CORPORATION, LTD.]

## N-Halogen Compounds. I. Decomposition of 1,3-Dichloro-5,5-dimethylhydantoin in Water at pH 9<sup>1</sup>

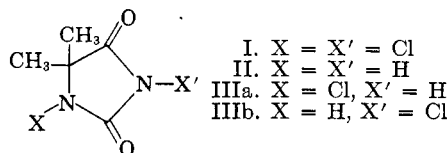
ROBERT C. PETTERSON AND URSZULA GRZESKOWIAK

Received March 9, 1959

When 1,3-dichloro-5,5-dimethylhydantoin(I) dissolved in water at pH 9, it decomposed rapidly and completely; 1-chloro-5,5-dimethylhydantoin(IIIa), *N*-chloroisopropylamine(IV), chloride ion, nitrogen, and carbon dioxide were the major products. Nitrogen chloride was a transient intermediate. *N*-chloro- $\alpha$ -aminoisobutyric acid (VIII) was shown to give mainly acetone, and not more than 12% of IV, on decomposition at pH 9, which excludes it as an intermediate. All known monochloro-5,5-dimethylhydantoin proved to be identical and are assigned the 1-chloro structure.

1,3-dichloro-5,5-dimethylhydantoin(I) is one of a number of *N*-halogen compounds under study in this laboratory with regard to their utility in powdered bleaching and disinfecting compositions. While several studies<sup>2,3</sup> of the hydrolysis of hydantoin in alkaline solutions have been made, none

has dealt with *N*-chloro derivatives except that of Biltz and Behrens<sup>3</sup> who made a few observations on 1,3-dichloro-5,5-diphenylhydantoin(V).



(1) Presented in part before the Organic Division at the New York Meeting of the American Chemical Society, September 1957.

(2) C. K. Ingold, S. Sako, and J. F. Thorpe, *J. Chem. Soc.*, 121, 1177 (1922); L. A. Cohen and E. M. Fry, *J. Am. Chem. Soc.*, 78, 5863 (1956).

(3) H. Biltz and O. Behrens, *Ber.*, 43, 1984 (1910).

It has commonly been assumed that weakly alkaline solutions of I, which are of interest for bleaching fabrics, contain only I and products resulting from hydrolysis of the N—Cl bonds,

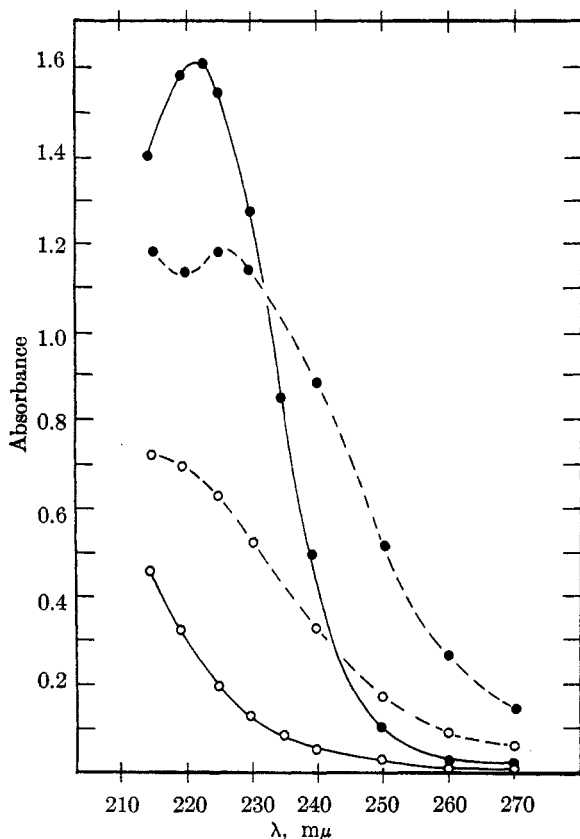


Fig. 1. Ultraviolet spectra of  $2.5 \times 10^{-4}M$  solutions of 1-chloro-5,5-dimethylhydantoin (---) and 5,5-dimethylhydantoin (—) in water (O) and in 0.01 *N* sodium hydroxide (●).

particularly hypochlorite ions. The present investigation commenced with the observation that large losses of active chlorine occurred rapidly when I was dissolved in water at pH 9.<sup>4</sup> The disappearance of active chlorine during the first hour at room temperature was found to vary greatly over the pH range of 3.2 to 12.7, being small at the extremes but reaching 50 to 60% in the region of pH 8 to 9 for  $5 \times 10^{-3}M$  solutions. The initial fast reaction near pH 9 was followed by a much slower decomposition which we have not investigated in detail. We have concentrated on identifying the major products of the initial reaction and estimating the amounts of them present, under one set of conditions. Unless otherwise noted the following discussion refers to the reaction of finely ground I with water at pH 9 (borate buffer) in the ratio of 1.97 g./1.( $10^{-2}M$ ) at room temperature over a 3.5-hr. period.

Depending on the degree of agitation, between 0.25 and 3.5 hr. elapsed before a clear solution was obtained; most of the decomposition seemed to occur during the process of dissolution. About 50% of the iodometrically titratable chlorine disappeared, and 2.5 moles of base was consumed by

(4) We are indebted to Mr. Charles P. McClain, who first observed this, for pointing it out to us.

the time the solution became clear. The lachrymatory odor of nitrogen trichloride was observed while the solid was dissolving, and its identity was confirmed by the ultraviolet spectra of solutions of the vapors. Nitrogen trichloride is unstable at pH 9, decomposing to nitrogen and hypochlorite and chloride ions.<sup>5</sup> By the time a clear solution was obtained nitrogen trichloride was no longer detectable.

A slowly stirred solution evolved 15% of the total nitrogen in the form of nitrogen gas in 3.5 hr., and another 10% in 5 weeks. At least part of this nitrogen presumably arose *via* nitrogen trichloride, little of which could escape under these conditions. The inactive chlorine after 3.5 hr. was all present as chloride ion, within experimental error. Carbon dioxide was present as carbonic acid ions.

The most puzzling phenomena associated with the decomposition of I at pH 9 were a peculiar pyridine-like odor found over the solutions after disappearance of all of the solid and the presence of bands near 2900, 1440, and 1370  $\text{cm.}^{-1}$  in the infrared spectrum of carbon tetrachloride solutions of the volatile components of these solutions. The responsible compound was finally isolated in a special experiment by distillation from a highly concentrated solution as a colorless, unstable, lachrymatory oil. This was proved to be the hitherto unknown *N*-chloroisopropylamine(IV) on the basis of: (i) iodometric chlorine determinations; (ii) elemental analysis; (iii) molecular refraction; (iv) decomposition in both acid and alkali to acetone and ammonia, with reduction of the (weakly) active chlorine atom; and (v) infrared absorption bands (see Experimental). Determination of the amount of volatile active chlorine, which seems to be due entirely to IV in the ordinary 3.5 hr.-old solutions, indicated that about 36% of I was degraded to IV. Limited attempts to prepare IV by conventional methods<sup>6</sup> were not successful.

The major product (63% yield), and the only nonvolatile active chlorine compound found present at 3.5 hr., was an *N*-monochloro-5,5-dimethylhydantoin(III), m.p. 145°. It was isolated quantitatively in almost pure form by extraction of an acidified solution with chloroform.

We could not determine from the literature whether III was the 1-chloro (IIIa) or 3-chloro (IIIb) derivative, or even if two different monochloro isomers were known. Rogers<sup>7</sup> described one, melting at 144–145° obtained by chlorination of 5,5-dimethylhydantoin(II), while Magill<sup>8</sup> obtained a monochloro compound, for which he reported m.p. 149–150°, by equilibrating an equimolar mixture of I and II. In our hands both procedures afforded good yields of the same

(5) R. M. Chapin, *J. Am. Chem. Soc.*, **53**, 912 (1931).

(6) A. Berg, *Ann. chim. et phys.*, [7] **3**, 289 (1894).

(7) A. O. Rogers, U. S. Patent 2,392,505, Jan. 8, 1946.

(8) P. LaF. Magill, U. S. Patent 2,430,233, Nov. 4, 1947.

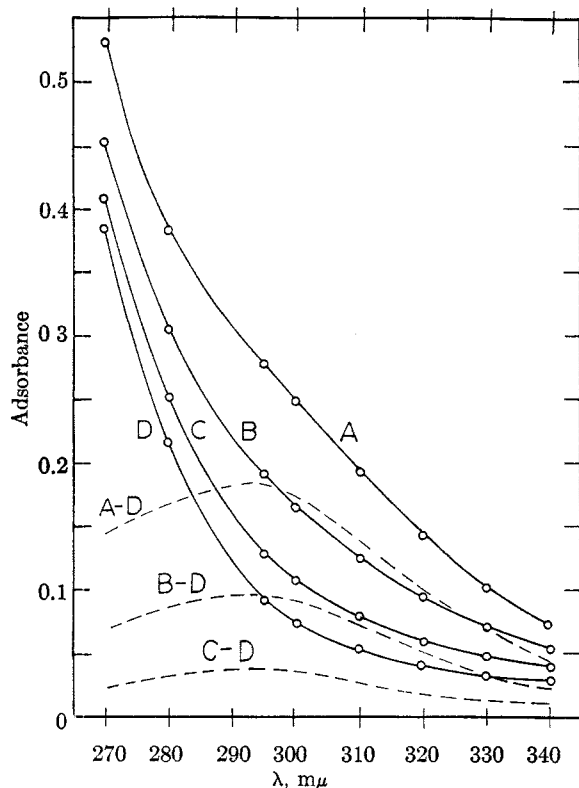


Fig. 2. Ultraviolet spectrum of a  $10^{-3} M$  solution of 1,3-dichloro-5,5-dimethylhydantoin after: A, 15; B, 45; C, 75, and, D, 165 to 195 min. Dashed lines show result of subtracting curve D from curves A, B, and C.

product, m.p.  $145^{\circ}$ ; identity with each other, and with our decomposition product, was established by mixture melting points, and by comparisons of their infrared and ultraviolet spectra.

The available evidence favors structure IIIa. The compound is a very strong acid for a hydantoin, since about one equivalent of sodium hydroxide is required to raise the  $pH$  of its solutions to 9; imides are generally more acidic than secondary amides. The ultraviolet spectrum of an aqueous solution of III showed a large bathochromic shift with increasing  $pH$  (see Fig. 1). Stuckey<sup>9</sup> has shown this to be characteristic of hydantoin having an unsubstituted imide group (*e.g.*, II). An aqueous solution of III at  $pH$  9 slowly lost active chlorine, and *N*-chloroisopropylamine(IV) was one of the decomposition products; this is most simply explained if the chlorine of III is on the 1-position. We conclude that the monochloro compound is 1-chloro-5,5-dimethylhydantoin(IIIa), and that the 3-chloro isomer IIIb has never been described.<sup>10</sup>

Of particular interest was the seeming absence of hypochlorite ion, which we could not detect in

$10^{-2} M$  solutions, although it would be expected to form by hydrolysis of I as well as by decomposition of nitrogen chloride. Certainly there can have been little of it at 3.5 hr. since the active chlorine remaining is fairly well accounted for as either IIIa or IV. Tests for chlorate ion and oxygen gas, products of its spontaneous decomposition,<sup>11</sup> were negative. Because of the importance of hypochlorite in bleaching, a search for it was made under varied conditions. No proof that it was formed in  $10^{-2} M$  solutions was found but some evidence for its presence as a transitory intermediate was obtained when the concentration of I was reduced to  $10^{-3} M$ . Subtraction of the ultraviolet absorption spectrum of a 2.75 hr.-old solution from that of fresher solutions gave difference curves characteristic of the hypochlorite ion ( $\lambda_{max}$  292  $m\mu$ , see Fig. 2) accounting, however, for not more than 25% of the total active chlorine. The 292  $m\mu$  peak in the difference curve disappeared rapidly and was entirely absent in 2.75 hr. The spectra of solutions of I made at  $pH$  10 and at  $pH$  13 both showed a well-defined shoulder in the 290  $m\mu$  region which suggests that more hypochlorite is formed at higher  $pH$ 's. Biltz and Behrens<sup>3</sup> believed, probably correctly, that 1,3-dichloro-5,5-diphenylhydantoin(V) hydrolyzed to the 1-chloro derivative and hypochlorite in dilute alkali, because they were able to recover much of the original V on acidification. In a similar experiment we recovered 65% of I on acidification of a 3% solution made from I and 1*N* sodium hydroxide. However, no I separated when a solution made at  $pH$  9 was acidified, which correlates with the essential absence of hypochlorite at  $pH$  9 in all but very dilute solutions.

Evidently at least two competing reactions, differently affected by  $pH$ , are involved here. In one, which predominates in highly alkaline solution, the dichloro compound I simply hydrolyzes to the 1-chloro derivative IIIa and hypochlorous acid. Both products will be completely ionized at high  $pH$ , and the ionized form of IIIa is probably relatively resistant to ring cleavage.<sup>12</sup>

The ring cleavage reaction is important in the neighborhood of  $pH$  9. There can be little doubt that some hypochlorite is always formed from I in aqueous solution, but when conditions are such that ring cleavage occurs, the hypochlorite is rapidly reduced to chloride in oxidizing the resulting hydrolysis products to molecular nitrogen and probably other products.

One of the intermediate hydrolysis products may be chloramide,  $NH_2Cl$ , which was not detected but is known<sup>13</sup> to be oxidized by hypochlorite to the observed  $NCl_3$ .

(9) R. E. Stuckey, *J. Chem. Soc.*, 331 (1947).

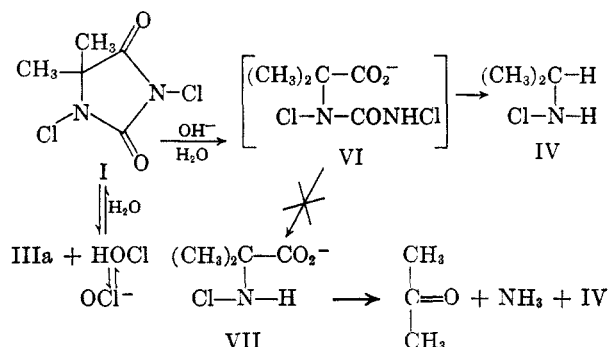
(10) A sample of "3-chloro-5,5-dimethylhydantoin" purchased from Bios Laboratories proved to be identical with our 1-chloro compound IIIa. C. G. Kamin mentioned the 3-chloro isomer IIIb in his U. S. Patent 2,441,360, May 11, 1948, but gave no properties; IIIa was probably meant.

(11) M. W. Lister, *Can. J. Chem.*, 34, 465 (1956).

(12) J. T. Edward and K. A. Terry, *J. Chem. Soc.*, 3527 (1957), have shown that succinimide and diacetylamine are probably cleaved by attack of hydroxide ion on the ionized forms of the imides.

(13) W. Marckwald and M. Wille, *Ber.*, 56, 1319 (1923).

One possible mechanism for the formation of *N*-chloroisopropylamine from I was tested and found wanting. Hydrolytic cleavage of I in the normal<sup>2</sup> manner would give the chlorinated hydantoic acid VI, which might either decarboxylate or lose its —CONHCl group to form *N*-chloro- $\alpha$ -aminoisobutyric acid (VII). The latter possibility could be checked by finding out if VII would decarboxylate cleanly to IV at pH 9 and room temperature. VII has never been isolated but is almost certainly formed when equimolar amounts of  $\alpha$ -aminoisobutyric acid and sodium hypochlorite react. Under the vigorous conditions used by Langheld<sup>14</sup> the product isolated from this reaction was acetone (75% yield), which is believed to have resulted from loss of chloride ion and carbon dioxide by VII, followed by hydrolysis of the isopropylideneimine thus formed. It was conceivable, however, that VII might be stable or decompose primarily to IV under our milder conditions. To test this possibility, buffered solutions of the amino acid and hypochlorite were mixed at room temperature to form a  $10^{-2}M$  solution of VII at pH 9. The active chlorine content of the mixture fell to 12% of its original value in 1 hr., then continued to decrease at a much slower



rate. During the first hour the formation and decomposition of VII was apparently complete, and the surviving 12% of the active chlorine was probably all in the form of *N*-chloroisopropylamine, which was qualitatively identified. In any case, not more than 12% of VII can have gone to IV. However, the major product (70–88%) was acetone as in Langheld's work. Since acetone was not found among the decomposition products of I, *N*-chloro- $\alpha$ -aminoisobutyric acid is not an important intermediate in the decomposition of I to IV. Since it has been shown that VII can decarboxylate to IV it is likely that VI, which has an even more electro-negative group *alpha* to the carboxyl group, would decarboxylate under these conditions.

A consequence of the rapid decomposition rate of I in alkaline solution is that stained cloth is bleached more effectively if the cloth is immersed in the bath before a formulation containing I is added than if the cloth is added to a solution made from I.

(14) K. Langheld, *Ber.*, **42**, 2360 (1909).

An investigation of the decomposition of di- and trichloroisocyanuric acids under similar conditions is in progress. These *N*-chloroimides have been found to undergo a similar ring cleavage reaction, albeit much more slowly than I, yielding finally cyanuric acid, nitrogen, chloride ion, and carbon dioxide; hypochlorite ion and nitrogen chloride are intermediates.

#### EXPERIMENTAL<sup>15</sup>

*Decomposition of I at pH 9. General method.* The 1,3-dichloro-5,5-dimethylhydantoin (I) used in this work was recrystallized from ethylene chloride and melted at 132° (lit.<sup>16</sup> 132°).

*Anal.* Calcd. for  $C_6H_8Cl_2N_2O_2$ : Active Cl, 35.99. Found: Active Cl, 35.99.

Except where noted, decomposition experiments were conducted by mixing finely ground I with an aqueous pH 9 buffer solution (made by adding about 2.14 l. of 0.5*M* sodium hydroxide to 5 l. of 0.5*M* boric acid solution) in the ratio of 1.97 g. of I per liter. The mixture was stirred at room temperature ( $23 \pm 2^\circ$ ) for about 3.5 hr., the solid dissolving in from 15 min. to 3.5 hr. depending on the amount of agitation. An initial rapid reaction involving reduction of some 50% of the active chlorine, and evolution of a gas with a lachrymatory odor, occurred during the dissolution. The nature of this decomposition was apparently little affected by the rate of dissolution (agitation). Most measurements were made at 3.5 hr. for convenience. Where buffer salts would interfere with product determinations, distilled water was used and the pH was held near 9 (pH meter) by continually adding sodium hydroxide solution, about 2.5 equivalents of base being required for the fast stage of the decomposition.

*The decomposition products. Nitrogen trichloride.* A solution of nitrogen trichloride in chloroform was obtained by passing nitrogen gas through an aqueous solution of  $NCl_3$  made from sodium hypochlorite by Chapin's method (a),<sup>9</sup> then through concentrated sulfuric acid, and finally into chloroform. Its ultraviolet spectrum closely resembled that of an aqueous solution<sup>17</sup> in general shape with  $\lambda_{max}$  at 342 and  $\lambda_{min}$  at 310  $m\mu$ .

Nitrogen was passed through a mixture of I (1.97 g.) and buffer solution (1 l.) and then through chloroform during the time needed for complete dissolution; the resulting chloroform solution of the volatile decomposition products was indistinguishable from that of the afore-described  $NCl_3$  solution in the 260–365  $m\mu$  region and had very strong absorption below 260  $m\mu$ . The solution contained 8% of the initial active chlorine.

*Nitrogen.* A flask was filled to the top with a mixture of I (1.97 g.) and borate buffer (1030 ml.), and quickly connected through a water-filled capillary to a gas burette containing water. Under mild agitation the solid dissolved during 3.5 hr. and 33.9 ml. of gas was evolved. Its volume was not detectably changed by contact with alkaline pyrogallol, acidified potassium iodide, or ammoniacal cuprous chloride; thus the gas contained no oxygen, chloroamines, or carbon monoxide, and is presumed to have been nitrogen. The yield

(15) Melting points are uncorrected. Elemental analyses, except for active chlorine, were done by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif. A Beckman Model DU spectrophotometer was used for the ultraviolet spectra; the infrared spectra were run by Mr. Everett Honorof on a Perkin-Elmer Model 21 spectrometer (sodium chloride prism).

(16) H. Biltz and K. Slotta, *J. prakt. Chem.*, **113**, 233 (1926).

(17) W. S. Metcalf, *J. Chem. Soc.*, 148 (1942).

was 15.1% of the total nitrogen of I; in a similar experiment lasting 5 weeks the yield increased only to 25%.

**Chloride ion.** In another run with 1.97 g. of I/1, in which only weak agitation was employed, a 50 ml. aliquot was removed after 3.5 hr., acidified with nitric acid, and treated with excess silver nitrate. The silver chloride (72.3 mg.) which separated contained 50.4% of the total chlorine. Iodometric titration of another aliquot showed that 49.7% of the chlorine was still active. A  $10^{-2}M$  solution of 1-chloro-5,5-dimethylhydantoin (IIIa) in the same buffer gave no precipitate when treated the same way.

**Carbon dioxide.** Qualitative identification was made on an unbuffered solution which had been held at pH 9 for 3.5 hr. by additions of sodium hydroxide. The colorless precipitate which separated when excess barium hydroxide solution was added was crude barium carbonate.

*Anal.* Calcd. for  $\text{BaCO}_3$ : Neut. equiv., 99. Found: neut. equiv., 101.

A 100 ml. portion of a similar solution, aged 5 weeks, was acidified with dilute sulfuric acid and heated to boiling while a stream of air was passed through it. The air was led into barium hydroxide solution where 0.1538 g. (39%, based on both C=O groups) of barium carbonate was formed.

***N*-Chloroisopropylamine (IV).** Passing nitrogen gas through solutions made from I at any time after the disappearance of the initial nitrogen trichloride odor removed a volatile substance containing active chlorine which could be absorbed in organic solvents; such solutions exhibited absorption bands at  $\lambda_{\text{max}}^{2,2,4\text{-trimethylpentane}}$  212  $\mu\mu$ .

The compound responsible was isolated in a special experiment in which a mixture of I (100 g.) and water (2 l.) was maintained near pH 9 by additions of sodium hydroxide until the solid disappeared (several hours). After 24 hr. at room temperature the solution (still at pH 9) was transferred to a simple distillation apparatus equipped with a cold finger containing a Dry Ice-acetone mixture. When the pot was warmed to 30° and the pressure reduced to 30 mm. a mixture of an oil and ice collected on the cold finger. Crude *N*-chloroisopropylamine separated as a colorless oil (yield, 23%, calcd. from active Cl) when the sludge melted. Nearly all of the dried (sodium sulfate, -5°, overnight) oil distilled through a short column at 33.5° (33.5 mm.) to give pure IV, a colorless oil with a pungent lachrymatory odor,  $n_D^{25}$  1.4468,  $d_4^{25}$  1.019,  $\lambda_{\text{max}}^{2,2,4\text{-trimethylpentane}}$  212  $\mu\mu$  (log  $\epsilon$ , 3.24). The infrared spectrum of the pure liquid showed bands at 2990, 2960, 2910, and 2860 m (NH, CH), 1630 and 1615 (N—H), 1430 and 1360 (CH<sub>3</sub>) and at 2720 vw, 2610 w, 2415 vw, 2300 vw, 2190 vw, 1235, 1144 w, 1115, 1078, 1058, 960 w, 816, 759 w, 695, and 665  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_3\text{H}_7\text{ClN}$ : C, 38.51; H, 8.62; N, 14.97; Active Cl, 37.90; MR<sub>D</sub>, 24.34. Found: C, 38.52; H, 8.62; N, 14.65; Active Cl, 37.74; MR<sub>D</sub>, 24.53. The active chlorine analysis was done iodometrically on a *t*-butyl alcohol solution of IV.

The conversion of I to IV in a  $10^{-2}M$  solution of I in 3.5 hr. was at least 25%, on the basis of the absorption at 212  $\mu\mu$  of a 2,2,4-trimethylpentane solution of the IV which could be blown out of the reaction mixture by an air stream. It was probably closer to 36%, estimated from the loss in active chlorine contents of a portion of the reaction mixture during rapid evaporation nearly to dryness *in vacuo* (rotating evaporator at 30°). The higher figure requires the reasonable assumption that IV was the only volatile active chlorine compound present in the solution.

Pure IV, stored over anhydrous sodium sulfate at -5°, lost about 1% of its active Cl in 12 days. A  $3 \times 10^{-2}M$  solution buffered at pH 9 for 39 days at room temperature in an amber flask, lost 33% of its active chlorine.

**Hydrolysis of IV to acetone and ammonia.** Attempts were made to reduce IV to isopropylamine by (a) treating IV (3 g.) with granular zinc (3 g.) and concentrated hydrochloric acid (25 ml.) for 5 hr., and (b) letting a mixture of IV (5 g.) and an excess of 0.25*N* sodium arsenite solution buf-

fered with sodium bicarbonate stand at 25° for 36 days. In both cases, when the resulting solutions were made strongly alkaline with sodium hydroxide and distilled the products were acetone, identified as its 2,4-dinitrophenylhydrazone, m.p. 124–125°, and ammonia (benzoyl derivative, m.p. 126–127°), which was apparently the only amine present.

When a carbon tetrachloride solution of IV was shaken with 50% hydrochloric acid, and allowed to stand for 24 hr., the organic layer developed a yellow color and very pungent lachrymatory odor, probably of *N,N*-dichloroisopropylamine,<sup>18</sup> while the aqueous layer proved to contain ammonia and acetone.

**1-Chloro-5,5-dimethylhydantoin (IIIa).** After 3.5 hr. a 200 ml. aliquot of a solution made from I in the usual manner was acidified with dilute sulfuric acid and extracted several times with 25-ml. portions of chloroform. Evaporation of the washed and dried (sodium sulfate) extracts gave 0.202 g. of colorless solid IIIa, m.p. 139–144°, yield, 63%. After a crystallization from ethylene chloride, the 1-chloro compound was pure, m.p. 144.5–145.0°, and showed absorption bands (Nujol) at 3230, 3080 m, 2703 w, 1778, 1740, 1350, 1296 m, 1137 w, 1086 m, 1078 m, 1048 w, 934 m, 795 w, 760 m and 663  $\text{cm}^{-1}$ , and  $\lambda_{\text{max}}$  (0.01*N* NaOH) 228  $\mu\mu$  (log  $\epsilon$ , 3.67). See Fig. 1.

*Anal.* Calcd. for  $\text{C}_5\text{H}_7\text{ClN}_2\text{O}_2$ : Active Cl, 21.81. Found: Active Cl, 22.00.

II (12.8 g.) was chlorinated by Rogers method,<sup>7</sup> yielding 12.0 g. (74%) of IIIa, m.p. 143–144°. Using a more convenient method of Magill,<sup>8</sup> II (13.4 g.) and I (19.7 g.) were stirred in 100 ml. of water at room temperature for 4 hr. to yield 30 g. (92%) of IIIa, m.p. 144.5–145.5°. Magill reported an 88% yield, m.p. 149–150°. Both of these products, on crystallization from ethylene chloride, melted sharply at 145°. The ultraviolet and infrared spectra of samples of IIIa obtained by all methods were identical and their melting points were not depressed by admixture with each other. When 0.1626 g. of IIIa ( $10^{-3}$  mole) was dissolved in 250 ml. of water, brought to pH 9 with 0.1*N* sodium hydroxide, and maintained at that pH for 2 hr., 10.3 ml. of the base was required; however, the active chlorine content decreased to 97.5% of its original value in the process.

When 2 g. of IIIa was dissolved in 500 ml. of buffer solution at pH 9 and allowed to stand at room temperature for 72 hr., *N*-chloroisopropylamine was formed. It was identified by its odor, and by the ultraviolet spectrum ( $\lambda_{\text{max}}$  212  $\mu\mu$ ) of the vapors blown out of the solution and collected in 2,2,4-trimethylpentane. Several aliquots were removed from a solution of IIIa (0.1702 g.) in borate buffer (250 ml.) kept at pH 9 and room temperature, and titrated for active chlorine. The cumulative losses of active chlorine at 1, 3, 5, 22, 46, and 92 hr. were respectively 1.8, 4.7, 6.3, 16.2, 18.8, and 46.7% of the original.

**Evidence for hypochlorite.** The ultraviolet spectrum of a  $10^{-3}M$  solution of I in borate buffer (pH 9) was determined as soon as possible (about 15 min. after the solid I was added to the buffer), and again at intervals up to 3.25 hr. Subtraction of the absorbance at 2.75 hr. (when changes had ceased) from earlier values gave difference curves resembling the spectrum of hypochlorite ion<sup>19</sup> (see Fig. 2). The magnitude of the difference at 295  $\mu\mu$  corresponds to a hypochlorite ion concentration of not over  $5 \times 10^{-4}M$  in the freshest solution measured, decreasing to zero by 2.75 hr. Useful difference curves were not obtained with  $10^{-2}M$  solutions of I; these required 30 min. to become clear, after which time only a small decrease in absorption with time could be observed.

When a fresh solution of I (3 g.) in 1*N* sodium hydroxide (100 ml.) was acidified with 10*N* sulfuric acid, 65% of the

(18) L. K. Jackson, G. N. R. Smart, and G. F. Wright, *J. Am. Chem. Soc.*, **69**, 1539 (1947).

(19) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

starting material was recovered as a colorless precipitate, m.p. and mixed m.p. 130–131°.

*Reaction of  $\alpha$ -aminoisobutyric acid with sodium hypochlorite.* The ultraviolet spectrum of a mixture made by adding a sodium hypochlorite solution to a suspension of  $\alpha$ -aminoisobutyric acid in water at 15° had a strong absorption maximum at 266 m $\mu$ , suggesting that acetone had been formed. The mixture was distilled in the manner described in the section on *N*-chloroisopropylamine, and the infrared spectrum of a dried carbon tetrachloride extract of the distillate was examined in a 0.1 mm. cell. The spectrum was exactly that expected of a mixture of *N*-chloroisopropylamine and acetone in this solvent. Bands characteristic of IV only were found at 2900 m, 2830 w, 1635 m, 1618 m, 1236, 1075 m, 1054 m, and 699 vs cm.<sup>-1</sup>, acetone bands were at 1720 vs, 1218 vs, 1089 w, and 897 w cm.<sup>-1</sup>, and bands due to both compounds appeared at 2980 m, 2940 m, 1436, and 1360 vs cm.<sup>-1</sup>

To a stirred solution of  $\alpha$ -aminoisobutyric acid (1.08 g.,  $1.05 \times 10^{-2}$  mole) in 500 ml. of 0.25*M* borate buffer (*pH* 9) was added dropwise (15 min.) a solution of sodium hypochlorite (0.745 g.,  $10^{-2}$  mole) in 500 ml. of 0.25*M* borate buffer at 23°. The clear solution, which had an odor of *N*-chloroisopropylamine, was allowed to stand at room temperature and aliquot portions were titrated iodometrically. After 5, 31, and 55 min., 2.5, 15, and 39 hr. there remained 36, 16, 12.8, 11.5, 11.0, and 8.9% respectively of the original active chlorine. The ultraviolet spectrum of the reaction

mixture after 23 hr. exhibited strong absorption below 240 m $\mu$ , presumably due to IV and the slight excess of  $\alpha$ -aminoisobutyric acid used, and a well-defined shoulder ( $\lambda_{\max}$  260,  $\lambda_{\min}$  247 m $\mu$ ) ending at 305 m $\mu$ , above which the solution was transparent. The shoulder must be caused by acetone (lit.<sup>20</sup>  $\lambda_{\max}^{0.04M}$  264 m $\mu$ ,  $\epsilon = 18.8$ ); its concentration may be estimated very roughly from the absorbance at 260 m $\mu$  (0.14) to be in the neighborhood of  $7.5 \times 10^{-2}M$  (75% yield). The conversion to IV in the first hour cannot have been more than about 12%, while that to acetone may have been 88% and was probably at least 70%. No indication of hypochlorite was found in the spectrum. During the first hour portions of the reaction mixture oxidized potassium iodide to iodine at *pH* 9, which hypochlorite will do, but after 1 hr., did not give iodine until acidified, which is typical of very weak oxidizing agents, including IV.

*Acknowledgments.* The authors are grateful to Dr. Robert C. Ferris for encouragement and for several helpful discussions, and to Herbert J. Becker, Lawrence A. Gemel, Charles P. McClain, and Morris Patapoff for valuable technical advice and assistance.

SOUTH GATE, CALIF.

(20) F. O. Rice, *J. Am. Chem. Soc.*, **42**, 731 (1920).

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY,<sup>1</sup> UNITED STATES DEPARTMENT OF AGRICULTURE]

## N-Methyl Amides of Phosphorus(V) Acids<sup>2</sup>

RICHARD L. ARCENEUX, J. G. FRICK, JR., ETHEL K. LEONARD, AND J. DAVID REID

Received March 9, 1959

A number of *N*-methyl amides of phosphorus (V) acids, have been prepared and characterized. Reactions involving thermal deamination and salt formation were studied on some of the compounds.

In the research conducted at the Southern Regional Research Laboratory leading to the development of flame-retardant finishes for cotton textiles, one phase of the work was directed toward the practical use of amides of phosphorus(V) acids. This report deals with the preparation and properties of some *N*-methyl amides of the acids which were studied during the course of this investigation. Most of the compounds have not been reported previously.

In general the amides were prepared by the addition of the acid chloride of a phosphoric or phosphonic acid to an excess of methylamine in inert solvent at reduced temperature under anhydrous conditions. The amine served also as an acid ac-

ceptor. The properties of the *N*-methyl amides which were prepared are shown in Table I. With the exception of *N,N'*-dimethyl-*P*-trichloromethylphosphonic diamide and *N,N',N''*-trimethylphosphorothionic triamide all of the amides are very soluble in water. Michaelis<sup>4</sup> has reported that the imido derivatives of phosphorothionic triamides have better organic solubility than the corresponding oxygen analogs. The same solubility relationship was found to hold for the sulfur-oxygen analogs examined in this investigation.

Michaelis<sup>4</sup> described the synthesis of *N,N'*-disubstituted phosphoramidic imides, with the structure RHN<sub>2</sub>P(O):NR, by the thermal decomposition of trisubstituted phosphoramides. These compounds were reported as being monomeric when the substituents are alkyl groups and dimeric when the substituents are aryl groups. The thionic analogs were reported to be monomeric also.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) This is a report on one phase of a program of research on the flame-resistant treatment of cotton textiles, being supported at the Southern Utilization Research and Development Division by funds supplied by the Air Research and Development Command, United States Air Force and conducted under the general supervision of the Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(3) J. R. Geigy A.-G., Brit. Patent 790,663, Feb. 12, 1958.

(4) A. Michaelis, *Ann.*, **407**, 290 (1915).