urated with 300 ml. of hot methanol, and again collected. The combined filtrates were acidified with methanolic hydrogen chloride and taken to dryness. When the residual gum did not solidify, it was dissolved in water and the base precipitated with sodium hydroxide and collected to give 6.9 g. of crude product, m.p. 80–90°. Recrystallization from water gave 2.7 g. (28% yield) of VIII, m.p. 118–120°.

Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 67.69; H, 8.72; N, 7.18. Found: C, 67.78; H, 8.91; N, 7.04.

A solution of 0.5 g. of VIII in 5.0 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 20 hr. and worked up as before to give 0.5 g. *dl, trans*-3-methyl-2-phenylmorpholine hydrochloride, m.p. 181–183°, undepressed upon admixture with a sample prepared from III.

***dl,cis*-5-Methyl-6-phenyl-3-morpholinone (IV).**—*dl*-Norephedrine (24.0 g., 0.160 mole) was added to a stirred suspension of 4.0 g. (0.172 mole) of sodium hydride (50% dispersion in mineral oil) in benzene at room temperature and stirring was continued for 30 min. The mixture was then cooled in an ice water bath and 20.0 g. (0.160 mole) of ethyl chloroacetate was added during 15 min. Stirring was continued for 1 hr. at room temperature and finally under reflux for 1.5 hr. The solution was cooled, diluted with ether, washed with dilute aqueous hydrochloric acid, dried over anhydrous sodium sulfate, and concentrated to a small volume. Boiling cyclohexane was added and the solution again concentrated and cooled to give 26.6 g. of crude product as colorless crystals, m.p. 120–135°. After three recrystallizations from benzene–cyclohexane the melting point was constant at 142–144°; yield 18.0 g. (59.3%).

Anal. Calcd. for $C_{11}H_{13}NO_2$: N, 7.33. Found: N 7.19.

***dl,cis*-3-Methyl-2-phenylmorpholine (V).**—Ten grams of IV was added in portions to a stirred suspension of 6.6 g. of lithium aluminum hydride in 600 ml. of ether. The mixture was stirred under reflux for 22 hr., then cooled and treated in succession with 6 ml. of water, 9 ml. of 10% aqueous sodium hydroxide, and 15 ml. of water. Anhydrous sodium sulfate was then added and the granular precipitate collected and washed well with ether. The filtrate was evaporated to dryness to 9.1 g. (98% yield) of a colorless oil which was characterized as the hydrochloride, m.p. 152–154° (recrystallized from absolute ethanol–ether).

Anal. Calcd. for $C_{11}H_{16}ClNO$: C, 61.81; H, 7.53; N, 6.55. Found: C, 62.21; H, 7.53; N, 6.64.

The picrate formed brilliant lemon yellow crystals from absolute ethanol, m.p. 210–211°.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: N, 13.33. Found: N, 13.70.

***dl,trans*-5-Methyl-6-phenyl-3-morpholinone (IX).**—The sodio derivative of *dl*-nor-ψ-ephedrine (8.3 g., 0.055 mole) was prepared and treated with ethyl chloroacetate by the procedure described above for IV. Crystals which had deposited in the benzene solution after standing overnight were redissolved by adding ether and methylene chloride and the solution was then worked up as before to give 9.3 g. (88% yield), m.p. 177–179° (unchanged upon recrystallization from benzene–cyclohexane).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.92; H, 7.00; N, 7.37.

Reduction of 1.00 g. of IX by the procedure described above for the *cis* isomer gave 0.86 g. (43% yield) of X as a colorless oil. The hydrochloride and picrate salts of this oil were identical (melting points, mixture melting points, and infrared spectra) with those of *dl, trans*-3-methyl-2-phenylmorpholine described above.

Acknowledgment.—The author is indebted to Mr. E. Conner of the Physical and Analytical Chemical Research Department for the microanalyses.

Some Substitution Reactions of Isovanillin and Related Compounds[1]

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Bromination of isovanillin results in substitution *ortho* and *para* to the phenolic function, and the reaction conditions determine to a considerable extent that position which undergoes substitution. The action of bromine on isovanillin acetate does not result in simple substitution of halogen for hydrogen, but some 5-bromoguaiacol acetate is formed. 5-Bromoisovanillin has been prepared, and some related reactions have been investigated.

Studies of substitution reactions of vanillin have been rather numerous,[2] but similar investigations involving isovanillin have been limited.[3–5] Several additional observations have now been made of the behavior of isovanillin and related compounds when subjected to bromination (and a nitration reaction has been carried out).

In the vanillin studies, it had been observed that the free phenolic group exerts the principal directive influence: substitution occurs chiefly at position 5 (*i.e., ortho* to the phenolic function). When the phenolic group of vanillin is acylated, the methoxy group exerts greater orienting influence than the acyloxy group, and in bromination reactions, particularly, substitution occurs exclusively at the position *para* to the methoxy group.[6] Nitration of vanillin acetate and of vanillin benzoate takes place *ortho* and *para* (chiefly *ortho*) to the methoxy group.[6b,7]

It was not lack of information concerning sub-

(1) This investigation was supported in part by the Washington State University Research Fund.

(2) See for example: W. B. Bentley, *Am. Chem. J.*, **24**, 171 (1900); H. D. Dakin, *ibid.*, **42**, 493 (1909); L. C. Raiford and J. G. Lichty, *J. Am. Chem. Soc.*, **52**, 4576 (1930); L. C. Raiford and E. H. Wells, *ibid.*, **57**, 2500 (1935).

(3) R. Pschorr and W. Stöhrer, *Ber.*, **35**, 4397 (1902).

(4) T. A. Henry and T. M. Sharp, *J. Chem. Soc.*, 2285 (1930).

(5) L. C. Raiford and M. F. Ravely, *J. Org. Chem.*, **5**, 204 (1940).

(6) (a) L. C. Raiford and W. C. Stoesser, *J. Am. Chem. Soc.*, **49**, 1077 (1927); (b) L. C. Raiford and J. E. Milbery, *ibid.*, **56**, 2727 (1934).

(7) R. Pschorr and C. Sumuleanu, *Ber.*, **32**, 3405 (1899); L. C. Raiford and W. C. Stoesser, *J. Am. Chem. Soc.*, **50**, 2556 (1928); S. F. McDonald, *J. Chem. Soc.*, 376 (1948).

TABLE I

BROMINATION OF ISOVANILLIN

Reaction no.	Isovanillin, g.	Bromine, g.	Solvent[a]	Reaction temp., °C.	Total reaction time, hr.	Total yield[b] Wt., g.	Total yield[b] %	Substituted isovanillin —% of total yield[b]— 2-Bromo[c,d]	6-Bromo[e,f,g]
1	5.0	5.5	Chloroform	60	1	5.11	67	25	75
2	5.0	5.79	Glacial acetic acid	105	1	5.27	69	41	59
3	5.0	5.3	Glacial acetic acid (+ sodium acetate)	105	1	5.44	72	83	17
4	5.0	5.3	Glacial acetic acid (+ sodium acetate)	23	1	5.34	70	100	0
5	5.0	5.79	Glacial acetic acid (+ sodium acetate)	23	12	5.20	68	100	0

[a] Vol., 30 ml. for isovanillin + 10 ml. for bromine; sodium acetate (5.4 g.) as indicated. [b] Average of two or more experiments (calcd. as anhydrous products). [c] Melting points observed for separated fractions: 1–2° ranges within 203–208° limits. [d] Melting points: purified product, 208–210° (lit.,[4] 211–212°); oxime, 172–173° (lit.,[5] 174–176°); acetate, 79–80° (lit.,[5] 82–84°). [e] Melting points observed for separated fractions of monohydrate: 1–2° ranges within 103–107° limits. [f] *Melting points*: purified product, 110° (lit.,[4] 112–114°); oxime 218–220° (lit.,[5] 224–226°); acetate, 105° (lit.,[5] 106–107°). [g] *Anal.* Calcd. for $C_8H_7BrO_3.H_2O$: C, 38.55; H, 3.61. Found: C, 38.61; H, 3.73.

stitution reactions of isovanillin and isovanillin derivatives alone which prompted this investigation; more important was the opportunity to determine what would result from the action of bromine on isovanillin acetate. The methoxy group (in position 4) should exert major directive influence. Although a methoxy group usually directs an entering bromine to a *para* position, in isovanillin acetate, the position *para* to methoxy is occupied by a formyl group, and it appeared possible, therefore, that the substitution might take place *ortho* to the methoxy group (at position 5).

When isovanillin was brominated,[4,5] substitution occurred at positions 2 and 6. In the work reported here, these results have been confirmed. However, in this more extended work, the results shown in Table I and in the Experimental indicate that the ratio of bromo isomers depends on the reaction conditions, although the reasons therefor are not clear.

It has been confirmed that isovanillin acetate is resistant to bromination under the usual conditions,[5] but in the presence of sodium acetate and an atmosphere of nitrogen, bromination gave a small amount of 5-bromoguaiacol acetate.[8] Whether this is (a) a direct displacement of the formyl group by bromine or (b) an indirect displacement involving oxidation of the aldehyde function to carboxyl followed by loss of carboxyl and introduction of halogen has not been determined. Changes of both types have been reported for related compounds; bromination of piperonal results in the displacement of the formyl group by halogen with the formation of some 1,2-dibromo-4,5-methylenedioxybenzene,[9] and bromination of 3-acetoxy-4-methoxybenzoic acid causes the replacement of carboxyl by halogen with the formation of 5-bromoguaiacol acetate.[5] This behavior of isovanillin acetate represents a striking example of the frequently noted influence of the methoxy group on the *para* position.

The action of bromine on isovanillin acetate was slow and of limited extent, and the change which did occur involved not simple substitution of halogen for hydrogen but displacement of a formyl group by a bromine atom; consistent with this were the observations that neither isovanillin triacetate nor isovanillin benzoate reacted when they were treated with bromine under the same conditions as those used with the acetate.

Because the action of bromine on isovanillin acetate failed to yield the 5-bromo compound, it was not possible to obtain previously unreported 5-bromoisovanillin by the hydrolysis of 5-bromoisovanillin acetate. The nitration of isovanillin acetate[3,5] has been repeated, and 5-nitroisovanillin acetate and 5-nitroisovanillin have been obtained; although some details differ from the data reported by Pschorr and Stöhrer,[3] these experiments confirm most of the observations in the prior reports. The attempt of Raiford and Ravely[5] to prepare this bromoisovanillin from the 5-nitro compound (followed by reduction and by a Sandmeyer reaction) had been unsuccessful; further attempts to accomplish this met with failure. However, 5-bromoisovanillin has been prepared: piperonal → protocatechualdehyde → 3-acetoxy-4-hydroxybenzaldehyde → 3-acetoxy-5-bromo-4-hydroxybenzaldehyde → 5-bromoisovanillin acetate (not isolated) → 5-bromoisovanillin.

One dibromoisovanillin has been prepared. 6-Bromoisovanillin monohydrate has been converted to 2,6-dibromoisovanillin; rather rigorous conditions were required to effect this change. It appears quite improbable that the substitution occurred at position 5, and it is concluded that the dibromo compound is the one named, but this has not been proved conclusively. Although efforts were made to isolate this compound as a product from the direct bromination of isovanillin, no dibromo product was obtained from reaction mixtures.

(8) E. M. Hindmarsh, I. Knight, and R. Robinson, *J. Chem. Soc.*, 941 (1917).

(9) A. M. B. Orr, R. Robinson, and M. M. Williams, *ibid.*, 947 (1917).

Experimental

Isovanillin.—This compound was obtained from the Monsanto Chemical Co., m.p. 112–114° (lit.,[10] m.p. 116–117°).

Bromination of Isovanillin.—The reaction was carried out under several different sets of conditions; the reaction mixtures were separated by fractional crystallization. The following (reaction no. 2) is illustrative of the general procedure used.

Isovanillin (5 g., 0.033 mole) was dissolved in 30 ml. of glacial acetic acid.[11] Approximately 0.15 g. of powdered iron was added, and the system was flushed thoroughly with nitrogen. A glacial acetic acid (10 ml.) solution of bromine (5.79 g., 0.0362 mole) was introduced during a 15-min. period (temperature, 105°); the mixture was stirred, and nitrogen flushing was continued for 45 min. (room temperature). Then the reaction mixture was poured into 200 ml. of water, which contained 2 g. of sodium bisulfite, and this mixture was allowed to stand overnight at 5°. Crude 2-bromoisovanillin[4] precipitated, was collected by suction filtration, and was crystallized from methanol–water (3:1) solution. The aqueous filtrate from which crude 2-bromoisovanillin had been separated was subjected to steam distillation (to remove acetic acid) and then extracted with ether. The ether extract was dried with anhydrous magnesium sulfate, and the solvent was removed by evaporation in a stream of air. Recrystallization of the residue from methanol–water (3:1) solution gave more 2-bromoisovanillin; addition of water to the methanol–water filtrate [to give a methanol–water (1:1) solution] precipitated 6-bromoisovanillin monohydrate.[4] (Further dilutions of the filtrate with water and recrystallizations of precipitates gave only very small amounts of starting material and acidic organic material.) The 6-bromoisovanillin monohydrate was recrystallized from methanol–water (1:1) solution.

Results of brominations of isovanillin under different reaction conditions are shown in Table I.

Isovanillin Acetate.—This compound was prepared in 85% yield by the method of Raiford and Ravely,[5] m.p. 87–88° (lit.,[5] m.p. 88–89°).

Bromination of Isovanillin Acetate.—Isovanillin acetate (6.38 g., 0.033 mole) was added to 30 ml. of glacial acetic acid containing 5.4 g. of anhydrous sodium acetate,[12] and 5.79 g. (0.0362 mole) of bromine dissolved in 10 ml. of glacial acetic acid was added dropwise during a period of 1.5 hr.; nitrogen was passed through the system throughout the reaction period. The reaction mixture was poured into 200 ml. of water containing 2 g. of sodium bisulfite, and this mixture was allowed to stand overnight at 5°. Fractional crystallization of the solid product from methanol gave 4 g. (62%) of starting material and 0.5 g. (6%) of 5-bromoguaiacol acetate, m.p. 64.5–65° and mixed m.p. with authentic material[8] 64°.

5-Bromoguaiacol Acetate.—This compound was prepared in 75% yield by the method of Hindmarsh, Knight, and Robinson,[8] m.p. 64–65° (from ligroin, b.p. 30–60°) (lit.,[8] m.p. 62–63°).

Isovanillin Triacetate.—This compound was prepared in 93% yield by a method similar to that used by Raiford and Ravely,[5] m.p. 120–121° (lit.,[5] m.p. 118–119°).

Attempted Bromination of Isovanillin Triacetate.—When attempts were made to brominate this triacetate by a procedure similar to that used for the acetate, starting material only was recovered from the reaction mixture.

Isovanillin Benzoate.—This compound was prepared in 82% yield by the method of Pschorr and Stöhrer,[3] m.p. 74–75° (lit.,[3] m.p. 75°).

Attempted Bromination of Isovanillin Benzoate.—When attempts were made to brominate this benzoate by a procedure similar to that used for the acetate, starting material only was recovered from the reaction mixture.

5-Nitroisovanillin Acetate.—To 36 g. of fuming nitric acid, which had been cooled to −10°, 10 g. (0.0515 mole) of isovanillin acetate was added in small portions. The mixture was allowed to stand for 20 min. at −5° and then poured onto 200 g. of crushed ice; the resulting mixture was allowed to stand overnight at 5°. The yellow solid was collected, washed repeatedly with water, and recrystallized from dilute methanol; this gave a yield of 4.1 g. (33%), m.p. 63–64° (lit.,[3] m.p. 86°[13]).

Anal. Calcd. for $C_{10}H_9NO_6$: N, 5.86. Found: N, 5.85.

The **phenylhydrazone of 5-nitroisovanillin acetate** was prepared and crystallized from 50% ethanol, m.p. 160–161° (lit.,[3] m.p. 165°).

Anal. Calcd. for $C_{16}H_{15}N_3O_5$: N, 12.77. Found: N, 12.85.

5-Nitroisovanillin.—5-Nitroisovanillin acetate was warmed in 5% sodium hydroxide solution until the solid was completely dissolved. The solution was cooled and acidified with dilute hydrochloric acid; the product was crystallized from *n*-heptane; this gave a 20% yield, m.p. 119° (lit., m.p. 119–120.5°[5] and 113°[3]).

The **phenylhydrazone of 5-nitroisovanillin** was prepared and crystallized from 25% ethanol, m.p. 166–167° (lit.,[3] m.p. 170°).

Anal. Calcd. for $C_{14}H_{13}N_3O_4$: N, 14.63. Found: N, 14.47.

Several attempts to reduce 5-nitroisovanillin with a number of reducing agents failed to yield 5-aminoisovanillin.

3-Acetoxy-4-hydroxybenzaldehyde.—Protocatechualdehyde was prepared[14] from piperonal and acetylated by the method of Pascu and v. Vargha[15]; it was crystallized from benzene, m.p. 109–111° (lit.,[15] m.p. 109–110°).

3-Acetoxy-5-bromo-4-hydroxybenzaldehyde.—3-Acetoxy-4-hydroxybenzaldehyde (5 g., 0.0278 mole) was added to a mixture of glacial acetic acid (30 ml.) and anhydrous sodium acetate (6 g.). A trace of iron powder was added, and flushing the system with nitrogen, which was continued during the reaction period, was started. Bromine (4.9 g., (0.0306 mole) dissolved in glacial acetic acid (10 ml.) was introduced dropwise over a 15-min. period; thereafter, the mixture was stirred at room temperature for 30 min. The reaction mixture was poured into 200 ml. of cold water, which contained 2 g. of sodium bisulfite, and this mixture was allowed to stand overnight at 5°. Crystallization of the solid from benzene gave a yield of 3.5 g. (49%), m.p. 168°.

Anal. Calcd. for $C_9H_7BrO_4$: C, 41.70; H, 2.70; Br, 30.89. Found: C, 41.55; H, 2.70; Br, 30.66.

As a derivative of the above, **5-bromoprotocatechualdehyde tetraacetate** was prepared by treating a small sample of the aldehyde with an excess of acetic anhydride and 2 drops of concentrated sulfuric acid; it was crystallized from dilute methanol, m.p. 107–108°.

Anal. Calcd. for $C_{15}H_{15}BrO_8$: C, 44.67; H, 3.72; Br, 19.85. Found: C, 44.88; H, 3.92; Br, 19.68.

5-Bromoisovanillin.—3-Acetoxy-5-bromo-4-hydroxybenzaldehyde (2.28 g., 0.0088 mole) was added to ether (30 ml.), and the mixture was cooled to 0°. A solution of diazomethane (prepared from 2 g. of nitrosomethylurea[16]) in ether was added dropwise, and the mixture was stirred for 15 hr.

(10) R. Wegscheider, *Monatsh.*, **3**, 792 (1882).

(11) In those experiments in which it was included, 5.4 g. of anhydrous sodium acetate was added at this point.

(12) When sodium acetate was omitted from the reaction mixture and the reaction was attempted in air rather than in an atmosphere of nitrogen, substitution did not occur; there was evidence of hydrolysis of starting material and of oxidation.

(13) It appears possible that in the report by Pschorr and Stöhrer[3] the melting points of isovanillin acetate and 5-nitroisovanillin acetate may have been (erroneously) interchanged.

(14) J. S. Buck and F. J. Zimmermann, "Organic Syntheses," Coll. Vol. II, J. Wiley and Sons, Inc., New York, 1943, p. 549.

(15) E. Pascu and L. v. Vargha, *Ber.*, **59**, 2821 (1926).

(16) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 844.

at 0°. The ether was evaporated in a stream of air, and a brown oil, which was insoluble in dilute sodium hydroxide solution, remained. The oil was mixed with 2% sodium hydroxide solution and refluxed for 30 min. The reaction mixture was acidified. The mixture was allowed to stand overnight, and the solid was crystallized from 50% ethanol; this gave 0.4 g. (20%) of product, m.p. 114–115°.

Anal. Calcd. for $C_8H_7BrO_3$: C, 41.56; H, 3.03; Br, 34.63. Found: C, 41.48; H, 3.07; Br, 34.41.

The **oxime of 5-bromoisovanillin** was prepared in quantitative yield by a standard procedure[17] and crystallized from water, m.p. 137.5–139°.

(17) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds" 3rd ed., J. Wiley and Sons, Inc., New York, 1948, p. 202.

Anal. Calcd. for $C_8H_8BrNO_3$: N, 5.69. Found: N, 5.45.

2,6-Dibromoisovanillin.—6-Bromoisovanillin monohydrate (5 g., 0.0201 mole) was brominated in glacial acetic acid by a procedure similar to that used for the bromination of isovanillin; reaction time, 11 hr. (reflux temperature). The product was crystallized from glacial acetic acid; yield was 2.1 g. (34%), m.p. 160–161°.

Anal. Calcd. for $C_8H_6Br_2O_3$: C, 30.97; H, 1.94; Br, 51.61. Found: C, 31.01; H, 2.06; Br, 51.83.

As a derivative of the above aldehyde, **2,6-dibromoisovanillin triacetate** was prepared in nearly quantitative yield by treating a small sample of the aldehyde with an excess of acetic anhydride and 2 drops of concentrated sulfuric acid and crystallized from methanol, m.p. 145–146°.

Anal. Calcd. for $C_{14}H_{14}Br_2O_7$: C, 37.00; H, 3.08; Br, 35.24. Found: C, 37.05; H, 3.39; Br, 35.06.

Steric Effects in the Baeyer Ditolylethane Synthesis

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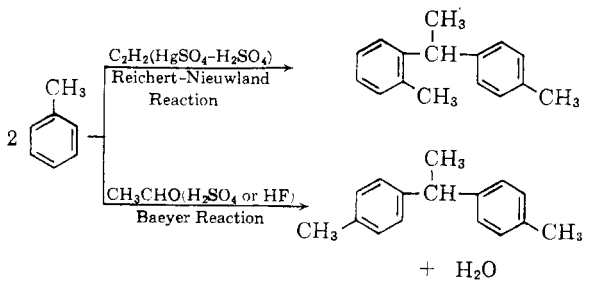
The effect of temperature on the isomer distribution of 1,1-ditolylethane from the Baeyer reaction has been examined. With paraldehyde as the alkylating agent, an increase in the ratio of 1,1-*p,p*-ditolylethane to other ditolylethane isomers is observed as the temperature is lowered. This temperature effect is not observed with acetaldehyde. The difference in the behavior between paraldehyde and acetaldehyde is believed to be due to differences in the steric requirements of the intermediate carbonium ions.

In an earlier publication[1] from these laboratories it was observed that the isomer distribution in 1,1-ditolylethane produced by the reaction of toluene in the Reichert-Nieuwland reaction with acetylene[2] differs greatly from that prepared in the Baeyer reaction with acetaldehyde.[3] The Reichert-Nieuwland product is predominantly 1,1-*o,p*-ditolylethane while the Baeyer product is predominantly 1,1-*p,p*-ditolylethane. Since the *para-para* isomer was



desired as an intermediate, a study was made of the Baeyer reaction in an effort to increase the proportion of this isomer in the product.

Acetaldehyde and paraldehyde have been used interchangeably heretofore in our laboratories for the Baeyer reaction with no noticeable differences in yields or in isomeric compositions of the ditolylethane produced. This result was assumed to arise from a rapid acid-catalyzed depolymerization of paraldehyde to acetaldehyde to give the same alkylating species in both cases.[4] It has now been found that at very low reaction temperatures there is a significant difference in the isomeric compositions of the products from paraldehyde and from acetaldehyde. At the usual reaction temperature of 0°, the compositions of the products are identical, both containing about 78% of the *para-para* isomer. When the reaction temperature is lowered to −78°, the amount of the *para-para* isomer is increased to 87% in the paraldehyde reaction, but remains unchanged in the acetaldehyde reaction. The experiments at the lower temperatures were conducted with hydrofluoric acid as the catalyst to avoid the difficulty of freezing of sulfuric acid at these temperatures. Table I summarizes the results of these studies.

We feel that these results can be explained by considering the steric requirements of the carbonium ions involved in the reaction. The acid-

(1) J. K. Dixon and K. W. Saunders, *Ind. Eng. Chem.*, **46**, 652 (1954).

(2) J. S. Reichert and J. A. Nieuwland, *Org. Syntheses*, **1**, 231 (1946).

(3) See O. Fischer, *Ber.*, **7**, 1193 (1874); O. Fischer and L. Castner, *J. prakt. Chem.*, [2], **82**, 280 (1910).

(4) The rate of depolymerization of paraldehyde in aqueous solutions of strong mineral acids is dependent on Hammett's acidity function H_0, with log k being linear in H_0 over the range of $H_0 = +1.4$ to -1.0 (R. P. Bell and A. H. Brown, *J. Chem. Soc.*, 774 (1954). If this linear relationship can be extended to 90% sulfuric acid with $H_0 = -8.27$, the first-order rate constant at 25° (the only temperature studied) is calculated to be 49,000 sec.$^{-1}$ with a half-reaction time of 1.4×10^{-5} sec. The rate in 90% hydrofluoric acid with $H_0 = -8.17$ (H. H. Hyman, M. Kilpatrick, and J. J. Katz, *J. Am. Chem. Soc.*, **79**, 3668 (1957), would be almost as rapid.