vacuo from a Claisen flask, carbon dioxide instead of air being bubbled through the flask. After a small forerun, which was discarded, 142.0 g. of pure tetra-allyl α-methyl glucoside distilled.

Unsaturation in allyl derivatives was determined by the Wijs method. Wijs solution was prepared as recommended by Kemp and Mueller.[10]

Free hydroxyl was determined by acetylating with pyridine–acetic anhydride (3:1) mixture and titrating the uncombined acetyl by a method to be published shortly by W. L. Porter, C. L. Ogg and C. O. Willits of this Laboratory.

Acknowledgment.—The assistance of Miss Esther M. Terry, who made the free hydroxyl and unsaturation analyses, is gratefully acknowledged.

Summary

The preparation and properties of tetra-allyl α-methyl glucoside are described. Polymerization of this compound in the presence of oxygen is discussed.

PHILADELPHIA, PA. RECEIVED JUNE 30, 1944

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[10] Kemp and Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF UNIVERSAL OIL PRODUCTS COMPANY]

The Dehydration of the Lower Aliphatic Alcohols in the Presence of Dilute Aqueous Solutions of Acids and Salts

BY V. N. IPATIEFF AND G. S. MONROE

In a previous investigation pertaining to the solubilities of various gases in aqueous alcoholic solutions, the observation was made that one of the alcohols employed underwent dehydration to the olefin. The magnitude of the reaction was so great that a systematic study of the lower aliphatic alcohols seemed justified on the grounds that a catalyst of unknown nature was probably present.

Alumina, as is generally known, is one of the best catalysts for the dehydration of alcohols[1] and can give good yields in the presence of small amounts of water. Other catalysts for the dehydration of alcohols have been described in the literature.

The dehydration of unsaturated alcohols (especially those with a secondary or tertiary hydroxyl group) with potassium acid sulfate, oxalic acid, or acetic anhydride has been discussed by Kyriakides.[2] Hibbert used iodine for the dehydration of the tertiary amyl alcohol to trimethylethylene, and also obtained tetrahydrobenzene from cyclohexanol with the same catalyst.[3] Volkow, using methyl iodide as a catalyst for the dehydration of monohydric alcohols, concluded that complete dehydration occurred with secondary and tertiary alcohols, while primary alcohols gave ethers.[4] Reppe and Trieschmann employed ammonium chloride, oxalic acid, or phosphoric acid in dilute 1,4-butylene glycol for dehydration to tetrahydrofuran.[5] The dehydration of alcohols of the terpene series with dilute aqueous salt solutions has been reported by Ipatieff and Pines.[6]

The present investigation of the dehydration of the lower aliphatic alcohols in the presence of dilute aqueous solutions of acids and salts began with the unexpected formation of isobutylene from tertiary butyl alcohol when heated with an equal weight of water at 200° in a rotating autoclave without any added catalyst. Repetition of the experiment gave the same results, over 80% of the alcohol going to the olefin. Further investigation revealed that the walls of the supposedly clean autoclave were contaminated with nickel chloride. When the experiment was repeated in another bomb with clean walls only 2% of the alcohol was dehydrated.

In the study of secondary butyl alcohol at 230°, no dehydration of the alcohol occurred in the presence of water alone or anhydrous hydrochloric acid. When dilute aqueous solutions of hydrochloric acid were employed in concentrations of 1.0% down to 0.02%, almost 84% of the alcohol underwent dehydration, about 81% to butenes and about 3% to polymer. The catalytic effect of the solution was still apparent when the concentration was reduced to 0.002%. In this case about 13% of the alcohol was dehydrated.

Dilute solutions of other strong acids, such as sulfuric, arsenic pentoxide (in the presence of water) or the salts of strong acids that dissolve or hydrolyze in water to give an acid reaction, such as potassium hydrogen sulfate or ferric chloride, likewise caused dehydration. Aqueous solutions of weak acids, such as carbon dioxide (in the presence of water), or acetic, had only a slight catalytic effect.

The fact that no olefin was produced from the alcohol in the presence of water alone or of anhydrous hydrochloric acid, while dilute aqueous hydrochloric acid solutions catalyzed the dehydration of about 84% of the alcohol to the olefin, indicates that the acid solution was the catalyzing agent. The low yields of olefins ob-

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[1] V. N. Ipatieff, *Ber.*, **34**, 3579 (1901); **36**, 1990 (1903).

[2] L. P. Kyriakides, THIS JOURNAL, **36**, 985 (1914).

[3] H. Hibbert, *ibid.*, **37**, 1748 (1915).

[4] A. Volkow, *J. Russ. Phys.-Chem. Soc.* **21**, 333 (1889); *J. Chem. Soc. Abs.*, **58**, 354 (1890).

[5] W. Reppe and H. G. Trieschmann (to General Aniline and Film Corp.) U. S. Patent 2,251,835 (August 5, 1941).

[6] V. N. Ipatieff and H. Pines, THIS JOURNAL, **66**, 816 (1944).

tained when solutions of weak acids were used show that the hydrogen ion was probably the specific catalyst.

Calculations show that when hydrochloric acid was present in the aqueous concentration of 0.002% (0.001 wt. % of alcohol plus water), under which condition 13% of secondary butyl alcohol was dehydrated, 1 molecule was surrounded by 10,000 molecules of alcohol and 40,000 molecules of water, a total of 50,000 molecules. It is interesting to compare these figures with an earlier investigation[7] of the hydrogenation of benzene with mixed copper catalyst containing different metal oxides. Pure copper was not a catalyst, nor was copper with 0.001% nickel when 1 atom of nickel was surrounded with 90,000 atoms of copper. With 0.1% nickel present, when 1 atom of nickel was surrounded by 900 atoms of copper, 10% of the benzene was hydrogenated.

Isopropyl alcohol followed the same general pattern of reaction as previously mentioned. When the aqueous solution was neutral to congo red but of *p*H 5–7, as much as 80% of the alcohol was converted to propene and about 3–4% was converted to polymer. When the aqueous solution possessed congo red acidity (*p*H range, 3–5), the dehydration was still high, almost 80%, but the dehydration was accompanied by varying amounts of polymer formation; in some cases 30–40% of the alcohol was converted to polymer. The *p*H of the solution was the major factor determining whether or not the dehydration was accompanied by substantial polymerization.

When the investigation was extended to cover the remaining lower aliphatic alcohols (methyl through butyl) it was found that methyl, ethyl, and normal propyl alcohols were converted to the corresponding ethers with little or no olefin formation, while normal and isobutyl alcohols dehydrated to olefins in the same manner as did isopropyl, secondary and tertiary butyl alcohols previously described.

Experimental Part

Apparatus and Procedure

The experiments were made in two high-pressure rotating autoclaves of 332-cc. and 875-cc. capacity. Some of the runs were made with the charge in direct contact with the walls of the bomb when the catalyst used would not react with the stainless steel surface of the bomb. In most of the runs, however, three types of glass liners were used: open, sealed, and vented with a capillary-sized opening in the closure. By the use of vented and open liners the catalyst was retained inside the liner so that it could not come into contact with the walls of the bomb. In those runs in which the catalytic effect of very dilute solutions of catalysts was studied, sealed glass liners were used, the pressure inside the liner being balanced by the required amount of similar charge outside the liner.

The heating period after reaching the desired temperature level was two to three hours.

The experimental conditions and results obtained for each experiment are summarized in Tables I–VII and in Figs. 1–3.

In these experiments, equal weights of alcohol and water were charged. The amounts of catalyst employed are specified in terms of weight per cent. concentration, including those which had limited solubilities in water. Yields are given as per cent. alcohol converted to olefin, to polymer, and to the corresponding ether.

Tertiary Butyl Alcohol.—The experiments with tertiary butyl alcohol were all made at 200°. No study of the effect of concentration was made, since the alcohol underwent dehydration to isobutylene to the extent of over 80% of the amount charged in the presence of minute quantities (almost traces) of nickel chloride.

TABLE I

DEHYDRATION OF TERTIARY BUTYL ALCOHOL TO ISOBUTYLENE AT 200°

Equal wts. of alcohol and water

Catalyst	Charge	Max. press., atm.	% Alcohol converted to C_4H_8	% Alcohol converted to Polym.
None[a]	Alcohol	24	5.3	0.0
None[a]	Alcohol + Water	22	2.3	.0
$NiCl_2$[b]	Alcohol + Water	112	84.5	.0
$NiCl_2$[c]	Alcohol + Water	100	82.5	.0

[a] Carbon steel autoclave with inactive surface. [b] Stainless steel autoclave with active surface owing to the presence of difficultly removable chlorides. Analysis of aqueous residue after removal of isobutylene indicated presence of 0.002% Ni^{++} and 0.006% Cl^-. [c] Catalytic effect still persisted after bomb had been extracted with water at 200° under pressure.

Secondary Butyl Alcohol.—The temperature employed in all experiments was 230°. In the presence of water alone and anhydrous hydrochloric acid no reaction occurred. Dilute aqueous solutions of strong acids or the salts of the same that hydrolyze to give comparable *p*H

TABLE II

DEHYDRATION OF SECONDARY BUTYL ALCOHOL WITH DILUTE AQUEOUS SOLUTIONS OF ACIDS AND SALTS AT 230°

Equal wts. of alcohol and water

Catalyst	Aqueous concn. wt., %	Type liner used	Max. press., atm.	% Alcohol converted to C_4H_8	% Alcohol converted to Polym.
None	. . .	None	42	0.0	0.0
HCl	1.0	Sealed	98	80.7[a]	3.9
HCl	0.1	Sealed	95	80.9	3.0
HCl	.02	Sealed	80	81.1	3.3
HCl	.01	Sealed	91	74.4	3.6
HCl	.002	Sealed	60	12.2	1.1
HCl	(No H_2O, 0.5% in alcohol	Sealed	42	0.0	0.0
H_2SO_4	1.2	Open	90	62.2[b]	2.5
As_2O_5	4.7	Capil.	72	52.5	2.9
CO_2	(25 atm.)	Capil.	78	3.3	0.0
CH_3COOH	2.9	Capil.	38	0.9	.0
$KHSO_4$	2.0	Capil.	78	49.3	1.7
$FeCl_3$	2.2	Sealed	83	82.7[c]	2.6
NaCl	2.0	None	43	0.0	0.0
Composition of butene, mole %			(*a*)	(*b*)	(*c*)
Propane			. . .	. . .	0.3
Isobutane			1.0	Trace	1.5
n-Butane				Trace	
1-Butene			9.5	18.5	10.6
2-Butene			87.0	80.9	85.0
Isobutylene			1.5	Trace	2.0
C_{5+}-Hydrocarbons			1.0	0.6	0.6

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[7] B. B. Corson and V. N. Ipatieff, *J. Phys. Chem.*, **45**, 431 (1941).

values were effective catalysts. Hydrochloric acid in the aqueous concentrations of as low as 0.002% still exerted a noticeable catalytic effect, about 13% of the alcohol charged undergoing dehydration, while at concentrations of 0.02–1.0% the conversion was in excess of 80%. Dilute aqueous solutions of weak acids, those with low ionization constants, were ineffective, never more than about 3% of the alcohol undergoing dehydration.

Isobutyl Alcohol.—Only one experiment was made with isobutyl alcohol at 240° in the presence of 1% ferric chloride solution. About 88% of the alcohol was dehydrated, 29% was converted to butenes and about 59% to polymer. Analysis of olefin showed that a substantial amount of *n*-butene was present. The formation of *n*-butene along with isobutylene also has been observed by various investigators in the dehydration of isobutyl alcohol over various catalysts. The olefin also contained about 10% *n*-butane, probably formed by hydrogenation of *n*-butene to *n*-butane from hydrogen produced by dehydrogenation of the alcohol.

TABLE III

DEHYDRATION OF ISOBUTYL ALCOHOL WITH FERRIC CHLORIDE SOLUTION AT 240°

Equal wts. of alcohol and water

Catalyst	Aqueous concn., wt. %	Type liner	Max. press., atm.	Initial N_2 press., atm.	% Alcohol converted to C_4H_8	Polym.
$FeCl_3$	1.0	None	300	0	29.1[a]	58.8

[a] Composition of butene, mole %.

C_3-Hydrocarbons	1.2
Isobutylene	51.8
n-Butenes	33.8
n-Butane	10.1
C_{5+}-Hydrocarbons	3.1

***n*-Butyl Alcohol.**—The dehydration of *n*-butyl alcohol with 0.9% ferric chloride solution was studied over a temperature range of 272–337°. Figure 1 shows the effect of temperature on dehydration. At the lower level, 2.1% of the alcohol was dehydrated to the olefin, while at 337°, 65.5% of the alcohol was dehydrated. The olefin product consisted of 21–23 mole per cent. 1-butene and 74–76 mole per cent. 2-butene, together with small amounts of other hydrocarbons.

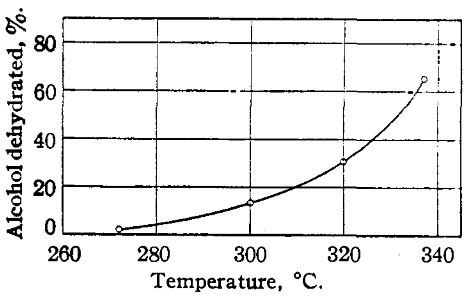

Fig. 1.—Effect of temperature on the dehydration of *n*-butyl alcohol to butene with 0.9% $FeCl_3$ solution (equal wts. of alcohol and water).

Isopropyl Alcohol.—Figure 2 shows the effect of concentration of hydrochloric acid (0.1–4.0%) and of hydrobromic acid (0.1–3.0%) on the dehydration of isopropyl alcohol at 275°. At the lowest concentration 0.1%, about 70% of the alcohol was dehydrated to propene and about 5% was converted to polymer. With increase in acid concentration, the olefin yield progressively dropped with a corresponding increase in polymer formation.

Figure 3 represents a temperature study of the dehydration of isopropyl alcohol with 2% magnesium chloride solution.

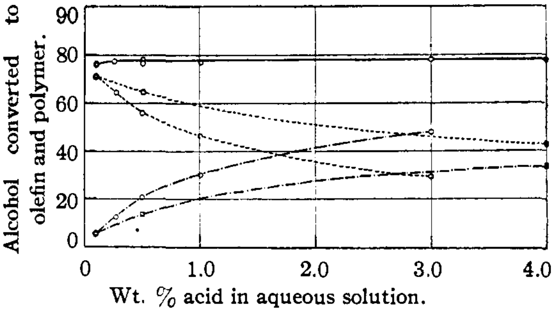

Fig. 2.—Effect of concentration of HCl and HBr on the dehydration of isopropyl alcohol at 275° (equal wts. alcohol and water); □——□, total % alcohol dehydrated (HCl); total % alcohol dehydrated (HBr); □----□, % alcohol dehydrated to propene (HCl); 0---0, % alcohol dehydrated to propene (HBr); □—-—□, % alcohol converted to polymer (HCl); 0—-—0, % alcohol converted to polymer (HBr).

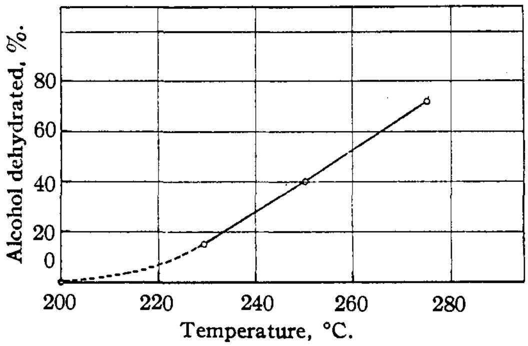

Fig. 3.—Effect of temperature on the dehydration of isopropyl alcohol to propene with 2% $MgCl_2$ solution (equal wts. of alcohol and water).

Table IV shows the results obtained with solutions of some salts of strong acids and weak bases that dissolve in water to give an acid reaction. Those solutions which developed congo red acidity (*p*H range 3–5) polymerized a relatively large amount of the propene formed. When

TABLE IV

DEHYDRATION OF ISOPROPYL ALCOHOL WITH DILUTE AQUEOUS SOLUTIONS OF SALTS OF STRONG ACIDS AND WEAK BASES AT 275°

Equal wts. of alcohol and water, capillary liner used

Catalyst	Aqueous concn., wt. %	Initial N_2 chgd., atm.	Max. press., atm.	% Alcohol converted to C_3H_6	Polym.	*p*H Solution, after expt.[a]
$CuCl_2$	3.5	25	150	36.6	31.8	3–5
$CuSO_4$	2.8	25	170	62.8	8.4	3–5
$HgCl_2$	4.0	25	160	58.8	21.8	3–5
$FeCl_3$	2.7	25	178	64.6	11.6	3–5
CuCl	4.0	25	185	68.0	3.2	5–7
$ZnCl_2$	4.0	25	182	72.3	3.3	5–7
$PbCl_2$	4.3	25	188	79.3	0.0	5–7
$NiCl_2$	2.3	25	180	78.5	1.1	5–7
$MnCl_2$	2.7	25	163	45.7	...[b]	5–7
$SnCl_4$	1.9	0	120?	84.0	3.2	5–7

[a] After propene and polymer were separated from reaction mass, the residual aqueous solution was tested with congo red (*p*H range 3–5). If neutral to congo red but acid to litmus, the *p*H was considered to be 5–7. [b] 4.1% of the isopropyl alcohol charged was converted to the corresponding ether.

TABLE V

DEHYDRATION OF ISOPROPYL ALCOHOL WITH 3.5% AQUEOUS CUPRIC CHLORIDE SOLUTION AT 275°

Equal wts. alcohol and water. Open *vs.* capillary vented liners, effect of nitrogen pressure.

Type liner	Initial N_2 press., atm.	Max. press., atm.	% Alcohol converted to C_3H_6	Polym.
Open	0	117	69.8	1.2
Capil.	0	105	36.7	39.2
Open	25	172	66.0	12.8
Capil.	25	150	36.6	31.8

TABLE VI

DEHYDRATION OF ISOPROPYL ALCOHOL WITH DILUTE AQUEOUS SOLUTIONS OF SALTS OF STRONG ACIDS AND STRONG BASES

Equal wts. of alcohol and water; capillary liner used.

Catalyst	Aqueous concn., wt. %	Temp., °C.	Initial N_2 chgd., atm.	Max. press., atm.	% Alcohol converted to C_3H_6	Polym.
Na_2SO_4	4.3	275	0	120	3.8	0.0
Na_2SO_4	4.3	325	0	185	8.8	.0
$CaCl_2$	2.0	275	25	158	15.0	.0
$CaBr_2 \cdot XH_2O$	3.2	300	0	162	37.6	.0
$BaCl_2$	3.6	275	25	152	7.8	.0[a]
$BaBr_2$	2.9	300	0	128	4.0	.0
$BaSO_4$	1.9	300	0	128	0.3	.0
NaBr	2.0	300	0	130	3.7	.0
NaI	2.0	300	0	128	0.0	.0
AgCl	1.9	275	0	82	1.0	

[a] 1.2% alcohol converted to the ether.

TABLE VII

DEHYDRATION OF METHYL AND ETHYL ALCOHOLS TO ETHERS WITH DILUTE AQUEOUS SOLUTIONS OF MAGNESIUM AND FERRIC CHLORIDES

Catalyst	Aqueous concn., wt. %	Mole ratio: $CH_3OH:C_2H_5OH:H_2O$	Temp., °C.	Max. press., atm.	% CH_3OH converted to Methyl ether	% CH_3OH converted to Methyl ethyl ether	% C_2H_5OH converted to Ethyl ether	% C_2H_5OH converted to Methyl ethyl ether
$MgCl_2$	3.0	0.56: 0 :1.00	370	63	2.8	—	—	—
$MgCl_2$	2.0	.56: 0 :1.00	370	296	56.2	—	—	—
$FeCl_3$	1.4	.56: 0 :1.00	360	324	61.2	—	—	—
$FeCl_3$	1.4	.56: 0 :1.00	380	302	59.8	—	—	—
$FeCl_3$	0.9	0 :0.26:1.00	350	272	—	—	30.2	—
$FeCl_3$	1.4	.23:0.24:1.00	370	310	22.7	17.8	11.9	17.9
$FeCl_3$	1.4	.15:0.32:1.00	370	328	13.1	32.8	23.7	16.4
$FeCl_3$	1.5	.23:0.24:1.00	400	322	26.4	18.7	8.1	18.7

the solution was neutral to congo red but acid to litmus, *p*H 5–7, dehydration was followed by only slight polymerization.

The polymerization of olefins was also influenced by the type of liners used. In capillary-vented liners, aqueous solutions of congo red acidity produced substantial polymerization as compared with relatively low yields of polymer in open liners. Table V compares the results obtained in the two types of liners. When the aqueous solutions were neutral to congo red, or had a *p*H of 5–7, polymerization never exceeded 3–4% of the alcohol charged, regardless of the type of liner used. The liner effect on polymerization is probably related in some way to diffusion.

Table VI tabulates results obtained with isopropyl alcohol and salts of strong acids and strong bases. Varying amounts of dehydration were obtained, calcium bromide at 300° giving a conversion of 37.6% of the alcohol to propene. Though these salts dissolve to give neutral solutions at room temperature it may be that at the high temperatures and pressures in the experiments, the *p*H of the solution changed to favor dehydration. The influence of temperature and pressure at the levels employed on the *p*H of solutions is not known.

***n*-Propyl Alcohol.**—*n*-Propyl alcohol departed from the usual pattern observed with the alcohols previously studied, in that dehydration stopped at the first stage—ether formation. In two experiments with 1.8% magnesium chloride solution, 1.6% of the alcohol was converted to *n*-propyl ether at 250° with no olefin formation, while at 255° 10.9% and 1.3%, respectively, of the alcohol charged were converted to the corresponding ether and olefin. It is probable that at higher temperatures the dehydration would pass through the ether stage and continue with olefin formation.

Methyl and Ethyl Alcohols.—Methyl and ethyl alcohols (Table VII) were investigated separately and together. The dehydration again stopped at the first stage—ether formation. The first two experiments with magnesium chloride were made at the same temperature, 370°, but at different pressures obtained by varying the amount of charge. At 63 atmospheres only 2.8% of the alcohol was dehydrated to the ether but at 296 atmospheres 56.2% was dehydrated, increased pressure apparently favoring the reaction. In the remaining runs with ferric chloride, methyl and ethyl alcohol, when charged alone, were converted to the respective ethers. When charged together the mixed methyl ethyl ether was formed along with substantial amounts of methyl and ethyl ethers.

Acknowledgment.—The authors wish to extend their appreciation to Mr. Lee Fisher and Mr. Charles Rohlfing for their assistance in this experimentation.

Summary

The dehydration of the lower aliphatic alcohols (methyl through butyl) has been studied under pressure in the presence of dilute aqueous solutions of acids and salts.

Anhydrous hydrochloric acid or water alone did not catalyze the dehydration reaction.

Dilute aqueous solutions of strong acids in concentrations up to about 5%, or salts that hydrolyze to give comparable *p*H values, catalyzed the dehydration of isopropyl and the butyl alcohols to olefins. Aqueous solutions of weak acids were only feebly catalytic.

When the *p*H range of the solution was 5–7, dehydration proceeded with only slight polymerization of the olefin. When the *p*H was at 3.5 (congo red range) or below there was a tend-

ency for the olefins formed to polymerize in substantial amounts.

Methyl, ethyl and *n*-propyl alcohols were dehydrated to the corresponding ethers with little or no olefin formation.

CHICAGO, ILL. RECEIVED JUNE 29, 1944

[CONTRIBUTION FROM THE LABORATORIES OF WALLACE & TIERNAN CO., BELLEVILLE, N. J.]

Substituted *p*-Aminobenzoic Acids

BY FRANZ CARL SCHMELKES[1] AND MARTIN RUBIN

The bacteriostasis brought about by the sulfonamides has been attributed to the competitive inhibition by these compounds of a metabolic process involving the essential nutrilite *p*-aminobenzoic acid.[2,3] Attempts have been made to correlate the bacteriostatic effectiveness of a given sulfonamide with its structural relationship to *p*-aminobenzoic acid.[4,5] It seemed of interest to us to investigate derivatives of *p*-aminobenzoic acid itself from this point of view. The bacteriological evaluation of the compounds prepared for this study has been reported elsewhere.[6] It is of interest that several of the non-sulfur containing compounds studied exhibited *in vitro* "sulfonamide" activity of the order of the active sulfonamides. That this bacteriostatic activity was in reality of the true "sulfonamide" type was indicated by its complete inhibition by *p*-aminobenzoic acid. During the course of this work the "sulfonamide" activity of *p*-aminobenzamide,[7] and *p*-aminophenyl ketones,[8] and other sulfur-free derivatives and analogs of *p*-aminobenzoic acid[9,10] was reported. The preparation of the new compounds reported in our previous study[6] is described below.

Of the various possible monohalogenated derivatives of 4-aminobenzoic acid, the only ones which have not been previously described were the 2- and 3-fluoro- and the 3-chloro-4-aminobenzoic acids. As the starting material for the 2-fluoro-4-aminobenzoic acid, 2-fluoro-4-nitrotoluene was prepared from diazotized 2-amino-4-nitrotoluene by the method of Schiemann.[11] It was observed that if all of the alcohol used in the preparation of the diazofluoborate were not carefully removed, partial deamination with formation of 4-nitrotoluene occurred on the thermal decomposition of the diazofluoborate. A similar deamination of a substituted benzidine by decomposition of a *bis*-diazofluoborate in absolute ethanol has been recorded.[12] Since traces of *p*-aminobenzoic acid interfere seriously with the "sulfonamide" assay of these compounds, it is essential that possible precursors of this material be eliminated in the preparation of the necessary intermediates.

Experimental Part

All melting points and boiling points are uncorrected.

2-Fluoro-4-nitrotoluene.—The diazofluoborate of 2-amino-4-nitrotoluene, prepared by the method of Schiemann from diazotized 2-amino-4-nitrotoluene[13] was washed with methanol and ethyl ether and dried by standing in a vacuum desiccator over phosphorus pentoxide overnight. Thermal decomposition in the usual manner[14] was best carried out on material that had been diluted with five volumes of sand. The product was extracted with ether, the ether extracts dried with anhydrous magnesium sulfate, concentrated, and the residue distilled, b. p. 65–68° (2 mm.); m. p. 34–35° from low boiling petroleum; yield 60%. *Anal.* Calcd. for $C_7H_6O_2NF$: C, 54.19; H, 3.90. Found: C, 54.76; H, 4.14. If the methanol was not completely removed from the diazofluoborate, the product of the thermal decomposition was difficult to crystallize. Oxidation of this material with neutral permanganate in the manner described below for the preparation of 3-chloro-4-acetamidobenzoic acid gave a mixture from which *p*-nitrobenzoic acid could be obtained on fractional crystallization from boiling water; m. p. 239–240°. There was no depression on mixed melting point with an authentic sample of *p*-nitrobenzoic acid. It is evident that the starting material was contaminated with *p*-nitrotoluene.

2-Fluoro-4-aminotoluene.—The reduction of 20 g. of 2-fluoro-4-nitrotoluene with tin and hydrochloric acid in the usual way gave 13 g. of 2-fluoro-4-aminotoluene (80.5%), b. p. 200–205°. *Anal.* Calcd. for C_7H_8NF: C, 67.18; H. 6.44. Found: C, 68.82; H, 6.92.

2-Fluoro-4-acetotoluidide.—The amine on treatment with acetic anhydride gave a quantitative yield of 2-fluoro-4-acetotoluidide which melted at 133.5–134° after recrystallization from water. *Anal.* Calcd. for $C_9H_{10}ONF$: C, 64.65; H, 6.03. Found: C, 64.67; H, 6.05.

2-Fluoro-4-acetamidobenzoic Acid.—Oxidation of 16.7 g. of 2-fluoro-4-acetotoluidide with neutral permanganate, as described below for the preparation of 3-chloro-4-acetamidobenzoic acid, gave 15.8 g. (80%) of the acid (m. p. 256–257°) on recrystallization from water. *Anal.* Calcd. for $C_9H_8O_3NF$: C, 54.82; H, 4.09. Found: C. 55.02; H, 4.19.

2-Fluoro-4-aminobenzoic Acid.—The hydrolysis of 10 g. of 2-fluoro-4-acetamidobenzoic acid was complete after twenty minutes of refluxing in 100 cc. of ethanol and 15 cc. of concentrated hydrochloric acid. After distillation of the

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(1) Deceased December 12, 1942.

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