TABLE I

ANALYSES AND PROPERTIES OF MANNICH BASES FROM PYRROLES AND AZOLES

Formula	Analyses, % N Calcd.	Found		M. p., °C.	B. p., °C. (mm.)		Product
$C_{10}H_{19}N_3$	23.18	22.99	22.92	.....	56–58 (2)	A.	2,5-bis-(Dimethylaminomethyl)-pyrrole[b]
$C_{14}H_{27}N_3$	17.70	17.60	17.50	.....	39–40 (1)	B.	2,5-bis-(Diethylaminomethyl)-pyrrole[c]
$C_{10}H_{16}N_2$	17.06	17.09	17.03	74.5–75.0	....	C.	2-(N-Piperidinomethyl)-pyrrole[d]
$C_{16}H_{27}N_3$	16.08	16.14	16.19	96.5–97.0	....	D.	2,5-bis-(N-Piperidinomethyl)-pyrrole[e]
$C_9H_{14}N_2O$	16.85	16.58	16.66	69.5–70.5	....	E.	2-(N-Morpholinomethyl)-pyrrole[d]
$C_{14}H_{23}N_3O_2$	15.84	15.80	15.78	86.5–87.0	....	F.	2,5-bis-(N-Morpholinomethyl)-pyrrole
$C_8H_8N_2O$	18.91	18.95	19.00	141–143	....	G.	1-Hydroxymethylbenzimidazole
$C_{18}H_{31}N_3$	14.52	14.46	14.42	157.0–157.5	....	H.	3,4-bis-(N-Piperidinomethyl)-2,5-dimethylpyrrole
$C_{11}H_{19}N_3$	21.74	21.63	21.56	.....	96–98 (2)	I.	3,5-Dimethyl-1-(N-piperidinomethyl)-pyrazole[f]
$C_{13}H_{17}N_3$	19.53	19.20	19.28	91.5–92.5	....	J.	1-(N-Piperidinomethyl)-benzimidazole[g]
$C_{12}H_{15}N_3O$	19.34	19.19	19.09	110.5–111.5	....	K.	1-(N-Morpholinomethyl)-benzimidazole[g]
$C_{12}H_{17}N_3$	20.67	20.71	20.66	.....	157 (3)	L.	1-Diethylaminomethylbenzimidazole[h]
$C_{12}H_{16}N_4$	25.90	25.64	25.69	92.5–93.5	....	M.	1-(N-Piperidinomethyl)-benzotriazole[i]
$C_{13}H_{18}N_4$	24.33	24.14	24.51	65.0–65.5	....	N.	1-(N-2′-Methypiperidinomethyl)-benzotriazole

[a] Water, 3 moles, also present. [b] $n^{25}D$ 1.4919, d^{25}_{25} 0.9406. [c] $n^{25}D$ 1.4812; d^{25}_{25} 0.9144; *MR* calcd. 75.43, found 75.57; hydrochloride, m. p. 124–127°; picrate, m. p. 112–114°; methiodide, m. p. 130°. [d] Hydrochloride and picrate unstable. [e] Hydrochloride, m. p. 119–122°; picrate, m. p. 184–186°. [f] $n^{25}D$ 1.4982; d^{25}_{25} 0.9919; hydrochloride, m. p. 238–240°. [g] Hydrochloride, decomposes before melting. [h] $n^{25}D$ 1.5657, d^{25}_{25} 1.0710. [i] Hydrochloride, m. p. 167–169°.

lowed to warm to room temperature. After two hours the ice-bath was restored and the mixture was neutralized slowly with 20% sodium hydroxide solution. The oily layer which separated crystallized on standing. It was recrystallized from acetone and formed white rosette-shaped groups of stout needles, m. p. 96.5–97.0°; yield 60 g. (92%); hydrochloride, m. p. 119–122° (dec. upon recrystallization); picrate, m. p. 184–186°.

1-(N-Morpholinomethyl)-benzimidazole.—Formalin, 9.6 ml., 38% (0.12 mole), was added, dropwise, to a cooled, stirred solution of 11.8 g. (0.10 mole) of benzimidazole and 9.6 g. (0.11 mole) of morpholine in 150 ml. methanol. After an hour the cooling bath was removed and stirring continued at room temperature for several hours. The solution was filtered, the ether evaporated, and the solid product recrystallized from acetone; yield, 21 g. (97%) of white platelets, m. p. 110.5–111.5°.

Summary

The Mannich reaction has been applied to various nitrogenous five-atom ring systems. A number of new derivatives of pyrrole, pyrazole, benzimidazole and benzotriazole have been prepared and described. The variations and limitations of the reaction in the heterocyclic series are discussed.

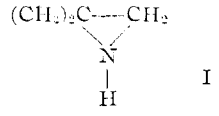
LAFAYETTE, INDIANA RECEIVED JUNE 26, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Compounds Derived from 2,2-Dimethylethylenimine

BY D. STANLEY TARBELL AND DAVID K. FUKUSHIMA[1]

Several workers[2] have investigated the possibility of obtaining optically active forms due to the trivalent nitrogen atom in suitably substituted ethylenimines. The most promising approach has been that of Cairns,[2b] who prepared 2,2-dimethylethylenimine (I) and obtained a crystalline urea derivative from it by the action of 1-α-phenylethyl isocyanate which, however, gave no evidence of separation into diastereoisomers on recrystallization.[3]



I

The presence of a carbonyl group on the nitrogen of the imine ring might tend to flatten the pyramidal arrangement of nitrogen valences, due to the contribution from resonance forms involving a carbon-nitrogen double bond. Therefore, in

(1) Present address: Research Laboratory, Memorial Hospital, New York City.

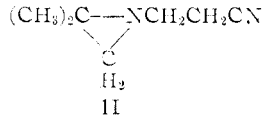
(2) (a) Adams and Cairns, THIS JOURNAL, **61**, 2464 (1939); (b) Cairns, *ibid.*, **63**, 871 (1941); (c) Mole and Turner, *Chem. Ind.*, 582 (1939); (d) Meisenheimer and Chou, *Ann.*, **539**, 70 (1939); (e) Maitland, *Ann. Rept. Chem. Soc. London*, **36**, 243 (1939).

(3) Prelog and Wieland, *Helv. Chim. Acta*, **27**, 1127 (1944) [*C. A.*, **39**, 4328 (1945)] have recently reported the resolution of Trögers base, in which the asymmetry is due to trivalent nitrogen atoms.

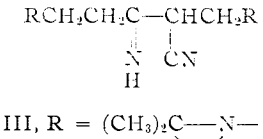
continuing work on this problem, we have attempted to prepare derivatives of I suitable for resolution in which this possibility of resonance structures involving the ring nitrogen would not be present. The present paper deals with the preparation of 1-(γ-aminopropyl)-2,2-dimethylethyleniminе (IV) and related compounds, and the results obtained so far are being reported because of recent active interest in ethylenimine derivatives.

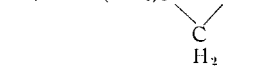
In the present work, numerous unsuccessful attempts were made to alkylate the imine I with methyl *p*-chloro-(or bromo)-methylbenzoate, using sodium carbonate or bicarbonate as the base. A run in which the imine was treated with a Grignard in the cold to form the N-magnesiochloride derivative before the addition of methyl *p*-chloromethylbenzoate was likewise unsuccessful.[4]

More promising results were obtained by adding the imine I to acrylonitrile, giving 1-(β-cyanoethyl)-2,2-dimethylethylenimine II[5]; the product, obtained in good yield, offered numerous possibilities for transformation to a substance useful for resolution purposes.[6] Treatment of II with the phenyl or methyl Grignard apparently yielded polymeric material instead of the desired ketones.



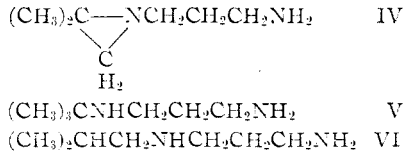
II



III, R = 

With butyllithium or phenyllithium a crystalline compound was obtained which was indicated by nitrogen content and molecular weight determinations to be the dimer III. It must have been formed by an intermolecular Thorpe reaction in the presence of the strongly basic lithium compounds.[7] It was not possible to obtain a crystalline semicarbazone from the dimer.

The reduction of the nitrile group of II to a primary amino group seemed to offer a more promising route to a compound suitable for resolution. The desired diamine IV was obtained in small yield by reduction with sodium and absolute alcohol[8] and in much better yield following Adams and Marvel,[9] using sodium and an absolute alcohol–toluene mixture.



IV

V

VI

At this point, it became necessary to prepare γ-*t*-butylaminopropylamine V for use in other work in this Laboratory on the synthesis of antimalarial drugs. In view of recent publications on the reduction of dimethylethylenimine I to *t*-butylamine with hydrogen and Raney nickel,[10] it was expected that II would undergo simultaneously reduction of the nitrile group and reductive cleavage of the imine ring to yield V, under these conditions. However, it was found that the product obtained from II on reduction with hydrogen and Raney nickel at 1500 lb. and 100°, using alcohol saturated with ammonia as solvent, was the same as that obtained from the sodium–alcohol reduction.

The structure assigned to IV is based on the analysis of the compound, of its dipicrate and dipicrolonate. The percentage composition of IV is appreciably different from that of V or VI, which might be formed by hydrogenolysis of the appropriate carbon-nitrogen bond in the ethylenimine ring. Furthermore, V was prepared by another method[11] and VI is described in this paper; the physical properties of these compounds and the melting points of their dipicrates show that IV is not identical with either of them.

The dipicrate of the imine IV could not be readily purified except by digestion with ethylene chloride. When the dipicrate was recrystallized from methanol, a different compound was obtained, with a much higher melting point. On the basis of carbon, hydrogen and nitrogen analyses, this compound must be VII; evidently picric

$(CH_3)_2C(OR)CH_2NHCH_2CH_2CH_2NH_2$, Dipicrate

VII, R = CH_3 VIII, R = H

acid catalyzes the cleavage of the imine ring with the addition of methanol. The acid-catalyzed hydrolysis of the imine ring is, of course, well-known, but the possibility that a similar process has occurred here, with the formation of VIII, is clearly ruled out by the analytical data.

Experiments on the resolution of IV, and on a general study of the reactions of II, IV and related compounds are actively under way. It is also planned to study the infra-red spectra of some of these ethylenimine derivatives.

(4) In work published since these experiments were carried out, Jones, Langsjoen, Neumann and Zomlefer, *J. Org. Chem.*, **9**, 125 (1944), found that the benzyl halides catalyzed the polymerization of ethylenimines; this may account for the poor results in our alkylation experiments.

(5) The addition of primary and secondary amines to acrylonitrile has been studied by Holcomb and Hamilton, THIS JOURNAL, **64**, 1309 (1942), and Whitmore and associates, *ibid.*, **66**, 725 (1944).

(6) An attempt to add the imine I to mesityl oxide yielded only starting material and an oil, presumably polymeric. In the addition of secondary amines to α,β-unsaturated ketones, the equilibrium is apparently unfavorable in some cases (Hochstetter and Kohn, *Monatsh.*, **24**, 774 (1903); Stewart and Pollard, THIS JOURNAL, **59**, 2006 (1937)).

(7) Ziegler, Eberle and Ohlinger (*Ann.*, **504**, 115 (1933)) reported the formation of iminonitriles analogous to III by the action of lithium diethylamide on aliphatic nitriles.

(8) Wohl and Berthold, *Ber.*, **43**, 2183 (1910).

(9) Adams and Marvel, THIS JOURNAL, **42**, 310 (1920).

(10) Karabinos and Serijan, *ibid.*, **67**, 1856 (1945); Campbell, Sommers and Campbell, *ibid.*, **68**, 140 (1946).

(11) Tarbell, Shakespeare, Claus and Bunnett, *ibid.*, **68**, 1217 (1946).

Acknowledgment.—We are indebted to Dr. T. L. Cairns for an invitation to work on this problem.

Experimental[12]

2,2-Dimethyl-1-(β-cyanoethyl)-ethylenimine (II).—A mixture of 22.5 g. of acrylonitrile and 20 g. of 2,2-dimethylethylenimine[2b] was refluxed for thirty-four hours. Starting material was removed by fractional distillation, and the residue yielded 23 g. (66%) of II, b. p. 79–83° (8 mm.). The analytical sample boiled at 198–199° (752 mm.), $n^{25}D$ 1.4428, d^{25}_4 0.9069.

Anal. Calcd. for $C_7H_{12}N_2$: N, 22.56. Found: N, 22.24.

The **picrate**, after recrystallization from ethylene chloride, melted at 109–110° if placed in the bath at 107°. If the sample was placed in the melting point bath at a lower temperature, the compound apparently would polymerize on prolonged heating and would not melt completely except at higher temperatures, where it would decompose.

Anal. Calcd. for $C_{13}H_{15}N_5O_7$: C, 44.18; H, 4.28. Found: C, 44.19; H, 4.42.

The action of the phenyl or methyl Grignard on the nitrile II yielded only undistillable oils or, in one case, a yellow powder which did not melt up to 250°.

Dimer of 2,2-Dimethyl-1-(β-cyanoethyl)-ethylenimine (III).—A solution of butyllithium (prepared from 0.4 g. of lithium wire, 3.5 g. of *n*-butyl chloride and 20 cc. of ether) was added dropwise (one-half hour) to a solution of 3.1 g. of 2,2-dimethyl-1-(β-cyanoethyl)-ethylenimine in 60 cc. of ether at room temperature. After stirring for an additional fifteen minutes, the mixture was treated with water, the ether solution separated, dried and the solvent removed under reduced pressure. A white solid (2 g., 64%) was obtained, of m. p. 73–83°, which, after recrystallization from ether, melted at 84–86°. The compound liquefied upon drying in a Fischer pistol over phosphorus pentoxide at room temperature, but solidified, m. p. 83–86°, after it was dissolved in ether and the solvent allowed to evaporate. It was recrystallized from ether and dried over potassium hydroxide.

Anal. Calcd. for $(C_7H_{12}N_2)_2$: N, 22.56. Calcd. for $(C_7H_{12}N_2)_2 \cdot H_2O$: N, 21.05. Found: N, 20.81.

The same product was obtained by treatment of II with methyllithium.

The molecular weight of the dimer was determined cryoscopically in benzene. The observed molecular weights, 212 and 216, were much higher than that of the monomer (124) but lower than that (266) calculated for $(C_7H_{12}N_2)_2 \cdot H_2O$. The benzene solution became turbid on cooling; this may have been due to the water of hydration, which might also explain the low observed molecular weights.

The **dipicrolonate** of the dimer, prepared in the usual manner, was recrystallized from ethanol and decomposed at 137°.

Anal. Calcd. for $(C_{17}H_{20}N_6O_6)_2$: C, 52.55; H, 5.19. Found: C, 52.49; H, 4.85.

No crystalline semicarbazone could be isolated.

The dimer was refluxed with 10% sodium hydroxide solution until the evolution of ammonia ceased. The presence of ammonia was demonstrated with Nessler's reagent. The dimer was unaffected by shaking for nine hours at room temperature with 5% sodium hydroxide solution. Acid hydrolysis of the dimer was not attempted due to the sensitivity of the imine rings to acid.

2,2-Dimethyl-1-(γ-aminopropyl)-ethylenimine (IV).—A. Method of Adams and Marvel.[9]—A mixture of 13 g. of sodium in 50 cc. of toluene was heated to boiling, and stirred until the sodium was finely divided. To this was added a solution of 10 g. of 2,2-dimethyl-1-(β-cyanoethyl)-ethylenimine (II) in 35 g. of absolute ethanol. The rate of addition was controlled to keep the solution boiling without external heating. When all of the sodium had dissolved, 150 cc. of water was added, the mixture cooled and the toluene layer separated. The aqueous layer was extracted twice with toluene, and the organic fractions combined and dried over potassium hydroxide. The ethanol and toluene were removed by fractional distillation. The distilland, containing water and the product, was saturated with potassium hydroxide, and the organic layer dried and distilled under diminished pressure. The product IV (6.5 g., 61%) was obtained, b. p. 80–84° (30–35 mm.). Another distillation yielded a colorless oil, b. p. 91–93° (50 mm.). The analytical sample after drying over potassium hydroxide and redistilling, had the following properties: b. p. 81.8° (25 mm.), $n^{20}D$ 1.4522, d^{24}_4 0.8615. γ-*t*-Butylamino-propylamine (V) has $n^{20}D$ 1.4431,[11] and the *i*-butyl isomer, as shown below, has properties differing from those of IV.

Anal. Calcd. for $C_7H_{16}N_2$ (compound IV): C, 65.57; H, 12.58. Calcd. for $C_7H_{18}N_2$ (γ-*t*-butylamino- or *i*-butylamino-propylamine, V or VI): C, 64.55; H, 13.93. Found: C, 65.80; H, 12.63.

The **dipicrate** could not be recrystallized unchanged from any solvent (see below), but was purified by repeated digestion with ethylene chloride. The picrate decomposed at 163.5–164.5° when placed in the melting point bath at 158°. If placed in the bath at a lower temperature, it would apparently polymerize and would not melt or decompose except at a much higher temperature. The dipicrate of γ-*t*-butylaminopropylamine (V) decomposed at 215–216°,[11] and the *i*-butylamino compound dipicrate (see below) melted at 171–172°.

Anal. Calcd. for $C_{19}H_{22}N_8O_{14}$: C, 38.90; H, 3.78. Found: C, 39.27; H, 3.65.

B. Method of Wohl and Berthold.[8]—To a hot solution of 25 g. of II in 350 cc. of absolute alcohol was added 30 g. of sodium in small portions during thirty minutes, after which the mixture was refluxed for one hour. The alcohol was removed by evaporation, water was added, and more alcohol removed. The aqueous layer was extraced with ether, the organic fractions combined and the solvents removed by fractional distillation. From the distilland was obtained 0.5 g., b. p. 160–165°, and 1.5 g., b. p. 165–170°, of the amine IV.

C. Reduction with Hydrogen and Raney Nickel.[13]—Compound II (50 g.) was reduced with Raney nickel in about 150 cc. of alcohol saturated with ammonia as the solvent; the mixture was shaken for one-half hour at about 100° and 1500 lb. pressure. After cooling, the contents of the bomb were washed out and the catalyst removed by filtration, using Superfiltrol to ensure complete removal. The filtrate was distilled at atmospheric pressure, and from the fraction boiling at 165–180°, 24.3 g. (47%) of the product was obtained by further distillation; it was a colorless oil, b. p. 169–172°, $n^{20}D$ 1.4523, and was shown to be identical with the material described in the previous paragraphs, by its physical properties and the behavior of its dipicrate.

D. Method of Graf.[14]—Reduction of 10 g. of II with chromous acetate[15] yielded only a trace of compound forming a picrate, which decomposed at 160°.

N-(β-Methoxy-*i*-butyl)-1,3-diaminopropane Dipicrate (VII).—2,2-Dimethyl-1-(γ-aminopropyl)-ethylenimine dipicrate (0.28 g.), whose melting point behavior is described above, was recrystallized from 10 cc. of methanol; yellow crystals (0.20 g.), m. p. 201–202° with some decomposition, were obtained, whose melting point was not changed by further recrystallization. The behavior of the product was entirely different from that of the starting material.

Anal. Calcd. for $C_{19}H_{22}N_8O_{14}$ (dipicrate of IV): C, 38.91; H, 3.78; N, 19.10. Calcd. for $C_{19}H_{24}N_8O_{15}$

(12) All melting points corrected; analyses by Robert Bauman, Carl Claus and the Micro-Tech Laboratories.

(13) We are indebted to Mr. John Melin and Mr. Mark Camp for the experiments on catalytic reduction.

(14) Graf, *J. prakt. Chem.*, [2] **140**, 39 (1934).

(15) Balthis and Bailar, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 1, 1939, p. 122.

(dipicrate of hydroxy compound VIII): C, 37.75; H, 4.00; N, 18.53. Calcd. for $C_{20}H_{26}N_8O_{15}$ (dipicrate of VII): C, 38.34; H, 4.24; N, 18.12. Found: C, 38.94, 38.83; H, 4.25, 4.19; N, 17.70, 17.82.

β-*i*-Butylaminopropionitrile.—Acrylonitrile (29 g.) was added dropwise with stirring to 40 g. of redistilled *i*-butylamine (b. p. 66.5–67.5°). After the addition was complete, the mixture stood for four hours at room temperature, was then refluxed for one hour, and stood overnight. Vacuum distillation yielded only a very small amount of starting material, and 62.97 g. (91%) of product was obtained, b. p. 82–88° (7 mm.). The analytical sample had the following properties: b. p. 107° (11 mm.), $n^{20}D$ 1.4352.

Anal. Calcd. for $C_7H_{14}N_2$: C, 66.62; H, 11.20; Found: C, 66.67; H, 11.03.

The phenylcarbamyl derivative, $(CH_3)_2CHCH_2N(CONHC_6H_5)CH_2CH_2CN$, was prepared by mixing 1 cc. of the propionitrile and 1 cc. of phenyl isocyanate in 10 cc. of petroleum ether. The product, which precipitated immediately in crystalline form, was best recrystallized from about 6 cc. of benzene, and melted, when recrystallized for analysis, at 117.5–118°.

Anal. Calcd. for $C_{14}H_{19}N_3O$: C, 68.53; H, 7.81. Found: C, 68.40; H, 7.75.

γ-(*i*-Butylamino)-propylamine (VI).—The corresponding nitrile (45 g.) was reduced by procedure C described above for II, and the product VI was obtained in 64% yield; the analytical sample had these properties: b. p. 95–97° (31 mm.); $n^{20}D$ 1.4452.

Anal. Calcd. for $C_7H_{18}N_2$: C, 64.52; H, 13.95. Found: C, 64.55; H, 13.66.

The **dipicrate** melted, after recrystallization from methanol, at 171–172°.

Anal. Calcd. for $C_{19}H_{24}N_8O_{14}$: C, 38.77; H, 4.11. Found: C, 38.31; H, 4.13.

Summary

2,2-Dimethylethylenimine has been added to acrylonitrile, and the product has been reduced, with sodium–alcohol, and with Raney nickel-hydrogen, to 2,2-dimethyl-1-(γ-aminopropyl)-ethylenimine. The evidence on which this structure is based is presented. The imine ring of the dipicrate undergoes methanolysis when recrystallized from methanol. γ-(*i*-Butylamino)-propylamine and several compounds related to it have been prepared and characterized.

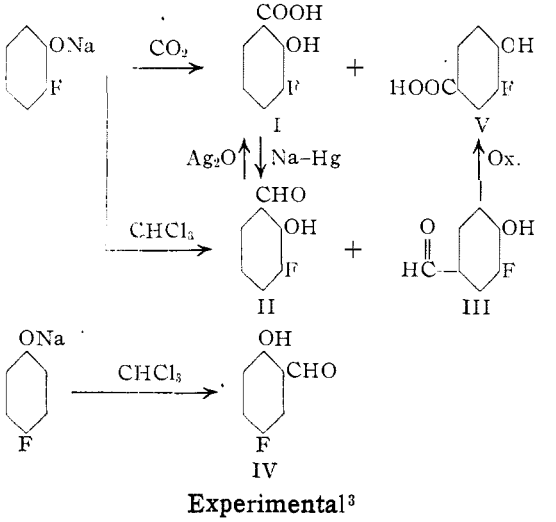
ROCHESTER, NEW YORK RECEIVED JULY 11, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

Some New Fluorinated Phenolic Aldehydes and Acids

BY LLOYD N. FERGUSON,[1] JAMES C. REID AND MELVIN CALVIN

In connection with the preparation of oxygen-carrying chelates,[2] it was desired to test 3-fluorosalicylaldehyde (II), and 5-fluorosalicylaldehyde (IV). 3-Fluorosalicylic acid (I) was prepared as an intermediate and 3-fluoro-4-hydroxybenzaldehyde (III) and 3-fluoro-4-hydroxybenzoic acid (V) were obtained as by-products according to the scheme



Experimental[3]

***o*-Fluorophenol** was prepared by the method of Schiemann.[4]

p-**Fluorophenol** was prepared by demethylation of Eastman Kodak Co. *p*-fluoranisole by refluxing for forty-eight hours with a four-fold *M* excess of 48% hydrobromic acid. The yield was 90%.

Preparation of 3-Fluorosalicyladehyde (II) and 3-Fluoro-4-hydroxybenzaldehyde (III) by the Reimer-Tiemann Reaction.—A solution of 77.2 g. (1.93 mole) of sodium hydroxide and 32.4 g. (0.29 mole) of *o*-fluorophenol in 260 ml. of water was brought to 55° and 76.8 g. (0.645 mole) of chloroform was run in during thirty minutes with efficient stirring, holding the temperature at 55°. After seventy minutes, the temperature was raised to 65° for an additional period of sixty minutes. The mixture was then acidified with sulfuric acid and steam distilled. Chloroform and unchanged phenol came out first, followed by solid II. When solid appeared, the receiver was changed and the pure product was collected. The hot residue remaining in the distillation flask was decanted away from a heavy tar on the bottom of the flask, and III crystallized out on cooling. An additional quantity of III was obtained by ether extraction of the mother liquor. Distillation of the recovered chloroform–phenol solution was carried out, reducing the pressure when the chloroform had been removed, and gave back 19.8 g. (61%) of the unchanged phenol in pure form. An additional quantity of II was obtained from the residue from this distillation by sublimation.

The yield of II was 5.3 g. (13%); white plates, m. p. 66.7–68.2° cor. *Anal.* Calcd. for $C_7H_5O_2F$: C, 59.98; H, 3.63. Found: C, 59.8; H, 3.80. The phenylhydrazone was prepared by the customary procedure, using phenylhydrazine in acetate buffer in alcohol at room temperature. Dilution with water threw down the phenylhydrazone as yellow plates; m. p. after recrystallization from dilute alcohol, 156.0–157.5° cor. The 2,4-dinitrophenylhydrazone was made in the usual way, using 2,4-dinitrophenylhydrazine in hot alcoholic hydrochloric acid solution. It was obtained as orange needles; m. p. after recrystallization from alcohol, 282–283° cor.

The yield of III was 6.1 g. (15%); white needles, m. p.

(1) Present address: Howard University, Washington, D. C.

(2) THIS JOURNAL, **68**, 2254, ff. (1946).

(3) All melting points are uncorrected unless otherwise noted.

(4) C. Schiemann, *Z. physik. Chem.*, **A156**, 397 (1931).