crude product (11.22 g.) with 250 ml. of hot water followed by filtration and then evaporation of the water from the filtrate on a steam bath gave 3.6 g. (77.8%) of succinimide, m.p. 118–122°, melting point undepressed on admixture with an authentic sample of succinimide, infrared spectrum superimposable upon that of an authentic sample of succinimide.

The water-insoluble solid was continuously extracted with benzene for 2 hr. There remained 4.24 g. (62.5%) of benzene-insoluble material which did not melt up to 400°. Its infrared spectrum was superimposable upon that of an authentic sample of diphenyltin oxide. An oxine derivative, prepared as described above, was identical to the oxine derivative of authentic diphenyltin oxide.

Orthoamides and Formamidinium Salts

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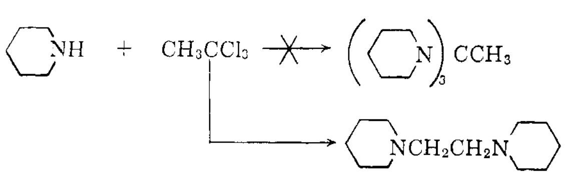
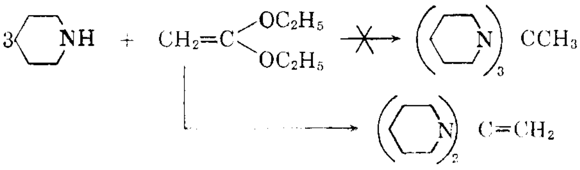
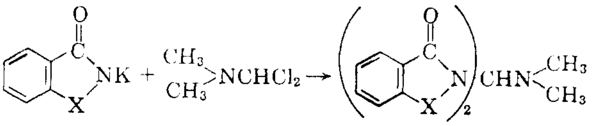
Several orthoformamides were prepared by the reaction of sodium salts of N-alkylanilines with chlorodifluoromethane. The orthoformamides, on treatment with mineral acids, alkyl or acyl halides give formamidinium salts in excellent yield. The formamidinium salts react with sodium hydride to yield methylenedianilines, with alkoxide ion to yield alkoxydiaminomethanes, and with phenyllithium to yield benzaldianilines. With primary amines they yield substituted formamidines and with sodium trichloroacetate they form trichloromethyldiaminomethanes. The formamidinium salts may also be nitrated in good yield.

The chemistry of 1,1,1-triaminoalkanes or orthoamides is not well known. In 1887 Kekule[1] reported that the reaction of piperidine with 1,1,1-trichloroethane produced 1,1,1-tripiperidinoethane. McElvain[2] also reported the synthesis of this compound by the reaction of ketenediethylacetal with piperidine.



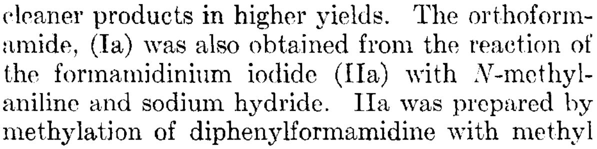


Bohme and Soldan[3] have recently re-examined the work of both of these authors and identified the compound reported by Kekule as 1,2-dipiperidinoethane and that reported by McElvain as 1,1-dipiperidinoethylene. They also prepared derivatives of orthoformamide by reaction of N,N-dimethyldichloroformamide with the potassium salts of phthalimide and saccharine.



Bredereck, *et al.*,[4] have also recently reported the synthesis of a series of triacyl orthoformamides.

By a variety of methods we have synthesized several triaryltrialkyl orthoformamides which were found to be readily convertible to a series of formamidinium salts.[5] The preferred method for preparing orthoformamides is the reaction of the sodium salt of an N-alkylaniline with chlorodifluoromethane. The reaction was found to be quite general and was applied to N-methylaniline, N-ethylaniline, and p-nitro-N-methylaniline to produce the series of orthoformamides, Ia–c.



Ia. $X = —H$ $R = —CH_3$
Ib. $X = —H$ $R = —C_2H_5$
Ic. $X = p\text{-}NO_2$ $R = —CH_3$

Chlorodifluoromethane was found superior to both dichlorofluoromethane and chloroform, producing cleaner products in higher yields. The orthoformamide, (Ia) was also obtained from the reaction of the formamidinium iodide (IIa) with N-methylaniline and sodium hydride. IIa was prepared by methylation of diphenylformamidine with methyl iodide and sodium hydride to give N,N'-diphenyl-N-methylformamidine followed by quaternization with methyl iodide in acetonitrile. This synthesis serves as compelling evidence for the assigned structures of both the formamidinium iodide (IIa) and the triaminomethane (Ia). It was found that

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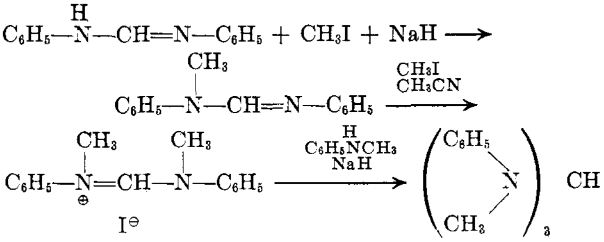
(1) A. Kekule, *Ber.*, **20**, 3247 (1887).

(2) H. M. Barnes, D. Kundiger, and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1281 (1940); **67**, 202 (1945).

(3) H. Bohme and F. Soldan, *Ber.*, **94**, 3109 (1961).

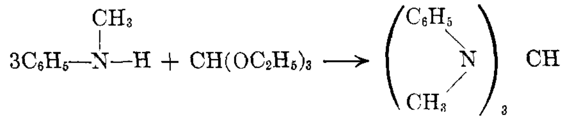
(4) H. Bredereck, R. Gompper, H. Rempfer, H. Keck, and K. Klemm, *Angew. Chem.*, **70**, 269 (1958); H. Bredereck, R. Gompper, H. Rempfer, K. Klemm, and H. Keck, *Ber.*, **92**, 329 (1959); H. Bredereck, R. Gompper, F. Effenberger, H. Keck, and H. Heise, *ibid.*, **93**, 1398 (1960).

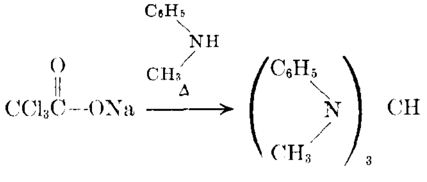
(5) For a brief preliminary account of the work see D. H. Clemens and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 2588 (1961).



IIa Ia

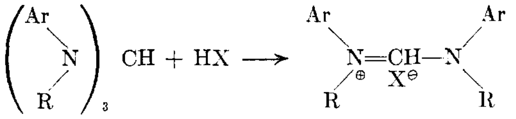
Ia could also be prepared by the treatment of ethyl orthoformate with N-methylaniline. Yields approaching 20% could be obtained in several hours at reflux or over a period of a month or more at room temperature; however, a considerable effort on our part failed to raise this yield. This method has the advantage of producing a very pure product, a fact that is of some importance in this particular case since the extreme insolubility of Ia makes it a difficult substance to purify. A final method of preparation of Ia was based on decomposition of sodium trichloroactate in an excess of N-methylaniline. This reaction, while convenient to run, also gives yields of around 20% and since it requires an excess of N-methylaniline as a solvent it is not particularly convenient for large-scale preparation. The initial step in this reaction may involve the formation of dichlorocarbene which then reacts further with N-methylaniline to produce the observed product. A simple displacement mechanism is equally attractive.





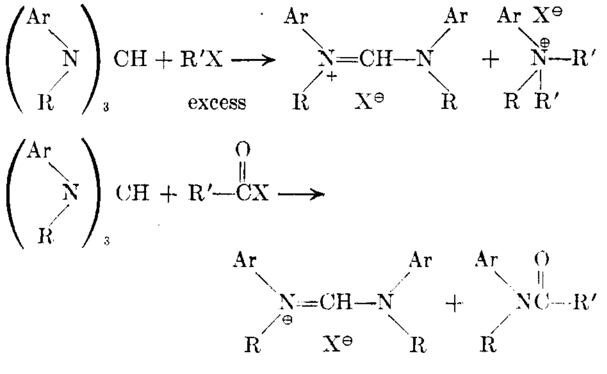
Several interesting facts were noted concerning this synthesis. All of the sodium trichloracetate is decomposed as indicated by a theoretical evolution of carbon dioxide, and yet essentially no N-methylaniline hydrochloride is formed. The chlorine not converted to sodium chloride is accounted for as chloroform which can be isolated in considerable amounts. Also it was found that the decomposition of trichloroacetic acid in N-methylaniline gives a good yield of chloroform and none of the orthoformamide. A likely explanation of these facts is that the hydrochloric acid initially formed in the reaction of N-methylaniline with sodium trichloroacetate rapidly converts the remaining sodium salt to the free acid, which then decomposes to chloroform and carbon dioxide. Though these results suggest that a higher yield of triaminomethane could be obtained in the presence of a strong base, no improvement in yield was noted when the decomposition was carried out in the presence of sodium hydride, sodium N-methylaniline or sodium acetate.

The most characteristic reaction of the triaminomethanes is their facile conversion to formamidinium salts. Several strong acids readily effect this transformation, and the main consideration is choice of an anion which gives a water-insoluble and thus easily isolated formamidinium salt. In some cases it is advisable to carry out the reaction in an acid which gives a soluble formamidinum salt and to add a second anion to precipitate the formamidinium cation. For example, Ia or Ib dissolve readily in concentrated hydrochloric acid to give a solution of the corresponding formamidinium chloride. On addition of potassium iodide to these solutions the formamidinium iodide immediately precipitates and can be readily isolated by filtration.

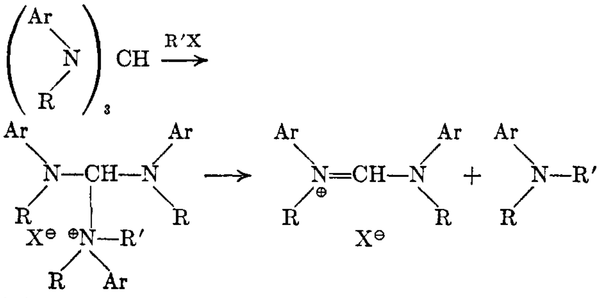


I II

Alkyl and acyl halides also convert the triaminomethanes to formamidinium salts. In this case the alkylated or acylated alkylaniline is also produced. In the case of the alkyl halide reactions an excess of alkyl halide was used and quaternary anilinium salt isolated. The reactions are particularly useful for preparing water-soluble formamidinium salts, since the transformation is carried out in an anhydrous medium and the products are easily separable.

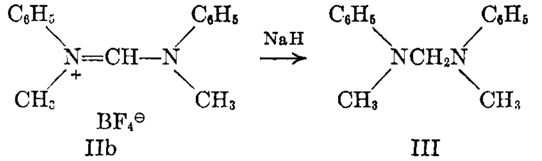


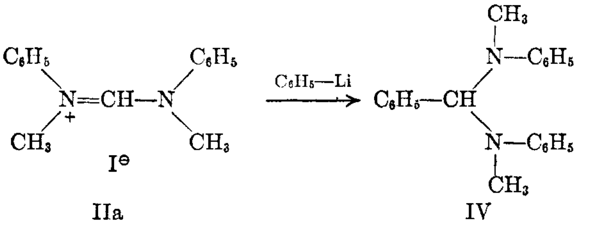
In each of the above preparations of formamidinium salts a positive charge is developed on one of the nitrogens of the orthoformamide. This charged intermediate then fragments to form the highly stabilized formamidinium salt and a second fragment, *i.e.*, the alkylaniline in the reaction with mineral acid, the dialkylaniline in the reaction with alkyl halides and the acylalkylaniline in the reaction with acyl halides. A concerted mechanism for this interconversion is an equally attractive possibility.



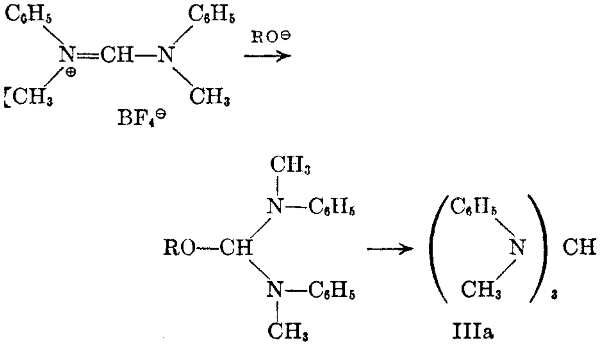
R′ = —H, -alkyl, or acyl-

The ready availability of the formamidinium salts has prompted us to study several of their reactions. These salts are subject to attack by a wide variety of nucleophilic reagents. IIb reacted readily with sodium hydride to give the diaminomethane (III) resulting from addition of hydride ion to the central carbon atom. This interesting reaction is one of the few cases known where sodium hydride smoothly reduces an organic compound. With phenyllithium a similar addition took place leading to the phenyldiaminomethane (IV) which was readily hydrolyzed to benzaldehyde. Unfortunately this reaction could not be generalized to include lithium alkyls. With *n*-butyllithium the only isolated product was the triaminomethane, Ia, accompanied by considerable tar.



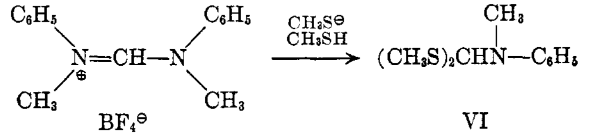


The addition of alkoxide ions to IIa produced a series of alkoxydiaminomethanes. These materials were quite stable in sealed vials in the refrigerator; however, on standing open to the atmosphere or on heating they were converted to the orthoformamide and a mixture of more volatile products which were not characterized.

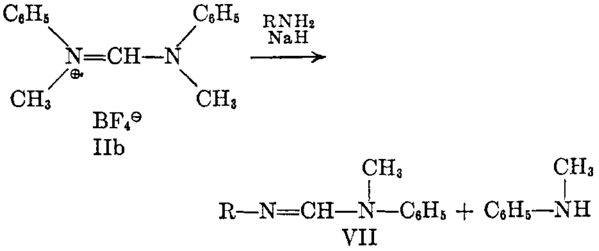


R = CH_3
R = i-C_3H_7
R = t-C_4H_9

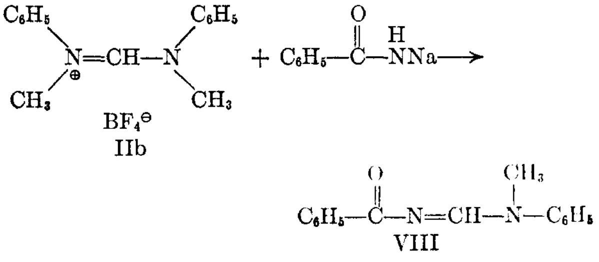
Surprisingly, the reaction of II with methyl mercaptide ion and excess methyl mercaptan produced the dimercaptoaminomethane (VI) which was quite stable at room temperature. A similar reaction using ethyl mercaptide ion produced a complex mixture of products which were not further characterized.



With primary amines good yields of substituted formamidines (VII) and *N*-methylaniline are obtained. Presumably these products result from elimination of *N*-methylaniline from the initially formed orthoformamide.

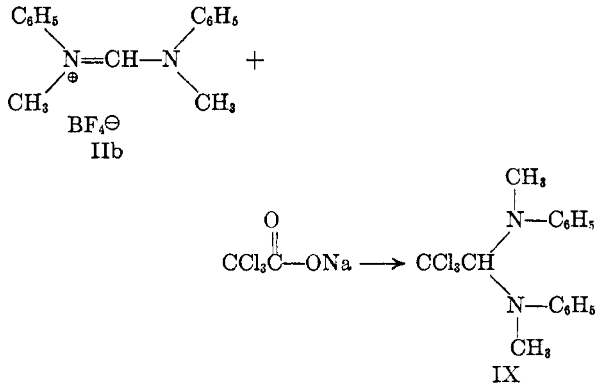


When R is phenyl the formamidine is accompanied by a small amount of the triaminomethane (Ia) which probably arises from addition of some of the initially formed N-methylaniline to IIb. A similar result is obtained when the sodium salt of benzamide is added to IIb. In this case the product is the *N*-benzoylformamidine (VIII).



With sodium trichloroacetate an interesting result is obtained. Rather than the expected trichloroacetate salt of IIb the product is the trichloromethyldiaminomethane (IX). Apparently the initially formed formamidinium trichloroacetate salt loses carbon dioxide to give the observed product.

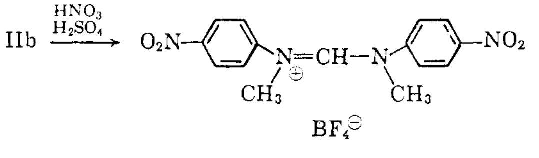
The formamidinium fluoroborate (IIb) was also nitrated in good yield by conventional mixed acid. The product was initially obtained as a mixed salt and was purified by recrystallization from 50% fluoboric acid. Surprisingly, the isolated product (63%) consisted entirely of the *para, para′* isomer, this being conclusively proved by hydrolysis to *p*-



IIb

IX

nitro-*N*-methylaniline and *p*-nitro-*N*-methylformanilide and by independent synthesis from the *p*-nitrophenylorthoformamide (Ic) and fluoboric acid. The relatively large amount of *p*-nitration is certainly indicative of the ability of the formamidinium halide group to function effectively as an electron-releasing substituent. As expected X is very susceptible to hydrolysis.



X

It is hydrolyzed slowly on exposure to the air and very rapidly in aqueous methanol. When kept in a desiccator, however, it is quite stable.

Experimental

***N*,*N*′,*N*″-Triphenyl-*N*,*N*′,*N*″-trimethyltriaminomethane from the Sodium Salt of *N*-Methylaniline and Chlorodifluoromethane.**—In a 3-l. three-neck flask fitted with a stirrer, a sealed gas inlet near to the bottom, a pressure equilized dropping funnel and a Dry Ice-cooled condenser were placed 700 ml. of 1,2-dimethoxyethane and 108 g. (2.25 moles) of a 50% dispersion of sodium hydride in mineral oil. A 25-g. portion of the *N*-methylaniline was added through the dropping funnel and the reaction mixture heated to reflux. After a 10-min. induction period gas evolution started and the remaining 215 g. of *N*-methylaniline (total 240 g., 2.25 moles) was added over a 15-min. period. Reflux was continued for an additional 15 min. To the hot solution of the sodium salt of *N*-methylaniline thus prepared gaseous chlorodifluoromethane was admitted through the gas inlet tube at such a rate that reflux was maintained. After 45 min. the refluxing vapors became cold and gas admission was stopped. 1,2-Dimethoxyethane (75 cc.) was added at this point to make the slurry stirrable and reflux was continued for 15 min. The precipitated solids were filtered by suction and washed with 200 cc. of 1,2-dimethoxyethane. The solids were slurried with 2 l. of water, heated 1 hr. on the steam bath, filtered, slurried with 1 l. of acetone, stirred 5 min. and filtered again. This process was repeated again and the finely divided crystalline product air dried to constant weight. The N,N′,N″-triphenyl-*N*,*N*′,*N*″-trimethyltriaminomethane weighed 144 g. (58%) and decomposed at 255–262°.

N,N′,N″-Triphenyl-N,N′,N″-triethyltriaminomethane.—In a 3-l. three-neck flask equipped with a stirrer, a sealed gas inlet to near the bottom, a pressure equilized dropping funnel and Dry Ice-cooled condenser were placed 400 ml. of 1,2-dimethoxyethane and 24 g. of a 50% dispersion of sodium hydride in mineral oil. Fifteen grams of *N*-ethylaniline was added through the dropping funnel and the reaction mixture heated to reflux. After 1 hr. of reflux gas evolution started and the remaining 45.6 g. of *N*-ethylaniline was added dropwise. Reflux was now continued until gas evolution became very slow. To the hot solution of the sodium salt of *N*-ethylaniline thus prepared chlorodifluoromethane was admitted through the gas inlet tube at such a rate that reflux was maintained. When the refluxing vapors became cold admission of gas was stopped and the reaction mixture cooled in ice and filtered. Volatile solvent was distilled from the filtrate and the remaining oil chilled overnight to crystallize 6.5 g. of product. The solids filtered from the reaction mixture were extracted with methylene chloride to obtain an additional 6.4 g. (total yield 12.9 g., 20.7%) of product. After recrystallization from 1,2-dimethoxyethane the *N*,*N*′,-*N*″-triphenyl-*N*,*N*′,*N*″-triethyltriaminomethane melted at 183–186°.

Anal. Calcd. for $C_{25}H_{31}N_3$: C, 80.38; H, 8.37; N, 11.25. Found: C, 80.13; H, 8.38; N, 11.03.

***N*,*N*′,*N*″-Tri-*p*-nitrophenyl-*N*,*N*′,*N*″-trimethyltriaminomethane.**—In a 1-l. three-neck flask, equipped with a stirrer, a gas inlet to near the bottom, a pressure equilized dropping funnel and a Dry Ice-cooled condenser were placed 500 cc. of 1,2-dimethoxyethane, 50.6 g. of *p*-nitrophenyl-*N*-methylaniline, and 16 g. of a 50% dispersion of sodium hydride in mineral oil. After heating to reflux gaseous chlorodifluoromethane was run in through the gas inlet tube until no more exothermic reaction was observed and the refluxing vapors became cold. The reaction mixture was filtered and the solid thus obtained slurried with 200 ml. of water, filtered, slurried with 200 ml. of 1,2-dimethoxyethane, filtered, and air-dried to give 12.2 g. (23.5%) of *N*,*N*′,*N*″-tri-*p*-nitrophenyl-*N*,*N*′,*N*″-trimethyltriaminomethane which began to darken at 230° and decomposed at 255–260°. A small sample was recrystallized from dimethylformamide. The purified sample began to sinter at 250° and decomposed at 260–265°.

Anal. Calcd. for $C_{22}H_{22}N_6O_6$: C, 56.64; H, 4.76; N, 18.02. Found: C, 56.30; H, 4.96; N, 17.73.

***N*,*N*′-Diphenyl-*N*-methylformamidine.**—A 14.4-g. (0.3 mole) sample of a 50% dispersion of sodium hydride in mineral oil was freed of mineral oil by washing with two 150-ml. portions of 1,2-dimethoxyethane. To this was added 150 ml. of 1,2-dimethoxyethane and 42.6 g. (0.3 mole) of methyl iodide. There was then added slowly a solution of 30 g. (0.15 mole) of *N*,*N*′-diphenylformamidine in 250 ml. of 1,2-dimethoxyethane. The reaction mixture was then heated to reflux and refluxing continued until 7.7 l. of hydrogen had been evolved as measured on a wet test meter. Water was added and the mixture extracted with methylene chloride. The methylene chloride layer was dried and distilled to yield 26.9 g. (85.5%) of *N*,*N*′-diphenyl-*N*-methylformamidine, b.p. 142–150° (0.1 mm.).

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.33; neut. equiv. 210. Found: C, 79.96; H, 7.15; N, 13.14; neut. equiv. 210.

***N*,*N*′-Diphenyl-*N*,*N*′,-dimethylformamidinium Iodide from *N*,*N*′-Diphenyl-*N*-methylformamidine.**—A mixture of 6.0 g. (0.028 mole) of *N*,*N*′-diphenyl-*N*-methylformamidine, 12.0 g. of methyl iodide, and 25 ml. of acetonitrile were heated under reflux for 3 hr. Another 12.0 g. of methyl iodide was then added and reflux continued for 16 hr. The solvent was distilled under reduced pressure until the product began to crystallize. Ice cooling followed by filtration yielded 7.0 g. (70%) of *N*,*N*′-diphenyl-*N*,*N*′-dimethylformamidinium iodide, m.p. 162–164°; λ_{max} C_2H_5OH 245 mμ (ε 21,000), shoulder 290 mμ (ε 3050).

Anal. Calcd. for $C_{15}H_{17}N_2I$: C, 51.15; H, 4.87; N, 7.96; I, 36.03. Found: C, 51.13; H, 5.11; N, 7.95; I, 35.95.

***N*,*N*′,*N*″-Triphenyl-*N*,*N*′,*N*″-trimethyltriaminomethane from *N*,*N*′-Diphenyl-*N*,*N*′-dimethylformamidinium Iodide.**—A 3.0-g. sample of a 50% dispersion of sodium hydride in mineral oil was washed by decantation with several portions of dry 1,2-dimethoxyethane. To this was added 100 cc. of dry 1,2-dimethoxyethane, 17.6 g. of *N*,*N'*-diphenyl-*N*,*N'*-dimethylformamidinium iodide, and 6 g. of *N*-methylaniline and the whole heated under reflux for 2 hr. The reaction mixture was cooled and filtered. The filtered solid was stirred with 50 cc. of water and filtered again to yield 7.3 g. (44%) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, m.p. 264–268° dec.

***N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane from Ethyl Orthoformate and *N*-Methylaniline.**—A mixture of 107 g. (1 mole) of *N*-methylaniline, 49 g. (0.33 mole) of ethyl orthoformate and 2 g. of *N*-methylaniline hydrochloride were placed in a stirred flask fitted with a short Vigreux column and a condenser arranged for distillation. The reaction mixture was heated for 4.5 hr. at 200–210° oil bath temperature while 13 g. of distillate, b.p. 70–80°, was collected. The product was isolated by filtration and after washing with acetone weighed 23 g. (20.8% yield) and melted at 265–275° dec.

***N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane from Ethyl Orthoformate and *N*-Methylaniline at Room Temperature.**—A mixture of 25 g. of ethyl orthoformate and 54 g. of *N*-methylaniline was allowed to stand in a stoppered flask for 33 days. Filtration and washing with acetone yielded 8.8 g. (16%) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, m.p. 270–275° dec.

Anal. Calcd. for $C_{22}H_{25}N_3$: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.43; H, 7.65; N, 12.82.

***N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane from Sodium Trichloroacetate and *N*-Methylaniline.**—A mixture of 106 g. (1 mole) of *N*-methylaniline and 37.2 g. (0.2 mole) of sodium trichloroacetate was heated to 145°. Carbon dioxide (5.2 l. at 25°) was evolved and passed through a Dry Ice–acetone trap before measuring. There was obtained in the trap 8.2 g. (34%) of chloroform, b.p. 62.5°. The reaction mixture was cooled, filtered, and the filtered solid slurried with water, filtered again, and washed with acetone to yield 14.8 g. (23.8%) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, m.p. 263–265° dec. The filtrate was distilled to dryness leaving only a very small dark residue.

Decomposition of Trichloroacetic Acid in *N*-Methylaniline.—In a 1-l. flask attached through a Dry Ice–acetone trap to a wet test meter was placed 107 g. (1 mole) of *N*-methylaniline and 32.7 g. (0.2 mole) of dry trichloroacetic acid. The mixture was heated until at 65° carbon dioxide began to be evolved and then heated slowly to a pot temperature of 180°. At this point 4.40 l. (corrected to STP) of gas was measured by the wet test meter. Theoretical is 4.48 l. A slight vacuum was then applied at a pot temperature of 50° to remove the last of the chloroform. The total yield of chloroform was 21.8 g. (91%).

***N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane from Chloroform and the Sodium Salt of *N*-Methylaniline.**—A mixture of 47.5 g. (1.0 mole) of a 52% dispersion of sodium hydride in mineral oil and 500 cc. of 1,2-dimethoxyethane was heated to reflux and 107 g. (1.0 mole) of *N*-methylaniline added at such a rate that the hydrogen evolution was not too rapid. After all the *N*-methylaniline was added and hydrogen evolution was very slow the reaction mixture was cooled to 30° and a solution of 40 g. (0.33 mole) of alcohol-free chloroform in 200 cc. of benzene added dropwise while keeping the temperature between 35 and 50°. When addition was complete the reaction mixture was heated to 85° over a 45-min. period, cooled, and filtered. The solid product was slurried with a little isopropyl alcohol to destroy a trace of unchanged sodium hydride, 1.5 l. of water added and the whole heated on the steam bath for 1 hr. and filtered. The product was then slurried in 1 l. of isopropyl alcohol, filtered, and air-dried to give 42 g. (38%) of *N*,*N*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, m.p. 276–280° dec.

***N*,*N'*-Diphenyl-*N*,*N'*-dimethylformamidinium Iodide.**—A mixture of 2.5 g. (0.015 mole) of potassium iodide, 8 cc. of concentrated hydrochloric acid, and 2.5 g. (0.0075 mole) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane was heated on the steam bath until all the triaminomethane had dissolved. An 8-cc. portion of water was added and heating continued until all the potassium iodide had dissolved. On cooling in ice there precipitated 1.7 g. (64.5%) of *N*,*N'*-diphenyl-*N*,*N'*-dimethylformamidinium iodide, m.p. 160–164°.

***N*,*N'*-Diphenyl-*N*,*N'*-diethylformamidinium Iodide.**—A 2-g. sample of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-triethyltriaminomethane was dissolved in 10 cc. of concentrated hydrochloric acid by warming. A 20-cc. portion of water was added followed by 6 g. of potassium iodide. After all the potassium iodide was dissolved the aqueous layer was decanted from the formed oil. Trituration of this oil with 100 cc. of water caused it to crystallize and it was recrystallized from a xylene–acetonitrile mixture to give 0.25 g. of *N*,*N'*-diphenyl-*N*,*N'*-diethylformamidinium iodide, m.p. 143–146°; λ_{max} C_2H_5OH 245 mμ (ε 19,000), shoulder 290 mμ (ε 2720).

Anal. Calcd. for $C_{17}H_{21}N_2I$: C, 53.69; H, 5.57; N, 7.37; I, 33.37. Found: C, 53.44; H, 5.72; N, 7.26; I, 32.95.

***N*,*N'*-Diphenyl-*N*,*N'*-dimethylformamidinium Fluoborate.**—In a 1-l. Erlenmeyer flask was placed 60 cc. of 48% fluoboric acid diluted with 200 cc. of water. To this was added 30 g. (0.09 mole) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane and the mixture heated 0.5 hr. on the steam bath at which time no more solid remained. Water (600 cc.) was added and heating continued for 1 hr. The temperature rose to 85° and only a little oil remained. The supernatant liquid was decanted through several layers of filter paper (to absorb any oil carried over) on a suction filter and the filtrate cooled slowly with scratching and seeding to a temperature of 45° and then cooled in an ice bath and kept below 3° for 1 hr. Filtration yielded 21 g. (75%) of *N*,*N'*-diphenyl-*N*,*N'*-dimethylformamidinium fluoborate, m.p. 115–118°. If desired this material may be recrystallized by dissolving it in 2 cc./g. of methylene chloride and adding 2.5 cc./g. of carbon tetrachloride. The recovery is 95% of material melting at 117–119°; λ_{max} C_2H_5OH 245 mμ (ε 24,000), shoulder 290 mμ (ε 4310).

Anal. Calcd. for $C_{15}H_{17}N_2BF_4$: C, 57.72; H, 5.49; N, 8.98. Found: C, 57.90; H, 5.29; N, 8.98.

***N*,*N'*-Diphenyl-*N*,*N'*-dimethylformamidinium Iodide from *N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane and Methyl Iodide.**—A mixture of 15 g. (0.0454 mole) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, 15 cc. of methyl iodide and 50 ml. of dry acetonitrile was heated under reflux for 18 hr. The reaction mixture was cooled to room temperature and filtered to obtain 8.7 g. (73%) of phenyltrimethylammonium iodide which was identified by comparison of its infrared spectrum with that of an authentic sample prepared from dimethylaniline and methyl iodide. On cooling in ice there crystallized 5.4 g. of *N*,*N'*-diphenyl-*N*,*N'*-dimethylformamidinium iodide, m.p. 160–162°. Concentration to 20 ml. and cooling gave an additional 6.9 g., m.p. 142–150°. The total yield was 12.3 g. (77%).

***N*,*N'*-Diphenyl-*N*,*N'*-dimethylformamidinium Bromide from *N*,*N'*,*N''*-Triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane and Ethyl Bromide.**—A mixture of 12.5 g. (0.0378 mole) of *N*,*N'*,*N''*-triphenyl-*N*,*N'*,*N''*-trimethyltriaminomethane, 20 cc. of ethyl bromide and 50 cc. of acetonitrile was heated under reflux for 18 hr. The solvent was distilled under reduced pressure leaving a partly crystalline mass which was slurried in ice-cold acetone and filtered to give 7.7 g. (95%) of *N*,*N'*-diphenyl-*N*,*N'*-dimethylformamidinium bromide, m.p. 143–148°. After recrystallization from acetone it melted at 147–149°, λ_{max} CH_3OH 243 mμ (ε 13,100), shoulder 290 mμ (ε 1560).

Anal. Calcd. for $C_{15}H_{17}N_2Br$: C, 59.02; H, 5.62; N, 9.18; Br, 26.18. Found: C, 59.11; H, 5.55; N, 9.09; Br, 26.01.

_N_,_N_'-Diphenyl-_N_,_N_'-dimethylformamidinium Bromide from _N_,'_N_,'_N_''-Triphenyl-_N_,_N_',_N_''-trimethyltriaminomethane and Acetyl Bromide.—A mixture of 9.96 g. (0.03 mole) of *N*,*N*',*N*''-triphenyl-*N*,*N*',*N*''-trimethyltriaminomethane, 50 cc. of 1,2-dimethoxyethane, and 4.0 g. (0.0325 mole) of acetyl bromide was stirred for 6 hr. The volatile solvent was distilled under reduced pressure, 75 cc. of reagent grade acetone added, and the mixture cooled in the refrigerator overnight. Filtration yielded 4.4 g. (48%) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium bromide, m.p. 145–149°. The filtrate was concentrated by distillation under reduced pressure and the remaining oil extracted with several portions of isoöctane. Concentration of the isoöctane extracts gave 4.4 g. (98%) of *N*-methylacetanilide.

_N_,_N_'-Diphenyl-_N_,_N_'-dimethylmethylenediamine.—A mixture of 75 cc. of dry 1,2-dimethoxyethane, 2.3 g. (0.048 mole) of a 50% dispersion of sodium hydride in mineral oil and 15 g. (0.048 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate were heated under reflux for 5 hr. Salts weighing 5.5 g. were filtered off and the filtrate distilled to give 7.2 g. (66%) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylmethylenediamine, b.p. 137–149° (1 mm.). A sample recrystallized petroleum ether (b.p. 30–60°) melted at 33–34° (reported[6] 35°).

Benzaldi-_N_-methylaniline.—A solution of phenyllithium in ether was prepared by the reaction of 0.15 g. of lithium wire and 1.57 g. (0.01 mole) of bromobenzene in 10 ml. of anhydrous ether. This was filtered through a small plug of glass wool into a separatory funnel and added to a suspension of 3.5 g. (0.01 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium iodide in 10 ml. of anhydrous ether. After stirring overnight the reaction mixture was filtered to remove suspended solid. The ether filtrate was added to a solution of 5 g. of sodium hydroxide in 35 ml. of water, layers separated and the aqueous layer extracted twice more with water. The combined ethereal extracts were dried over magnesium sulfate and the ether distilled under vacuum, leaving 1.5 g. (71%) of crystalline benzaldi-*N*-methylaniline. After recrystallization from ethyl acetate it melted at 127–130°.

Anal. Calcd. for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33; N, 9.27. Found: C, 83.17; H, 7.37; H, 9.40.

A small sample of benzaldi-*N*-methylaniline gave benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 230–234°, on treatment with 2,4-dinitrophenylhydrazine reagent. This gave no depression on admixture and melting with an authentic sample.

The Reaction of _n_-Butyllithium with _N_,_N_'-Diphenyl-_N_,_N_'-dimethylformamidinium Fluoborate.—To a mixture of 12.5 g. (0.04 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate and 150 cc. of dry 1,2-dimethoxyethane was added 25 cc. of *n*-butyllithium solution in heptane (0.001615 equivalent per cc., 0.04 mole). After stirring for 0.5 hr. the reaction mixture was filtered. The filtered solids were slurried with 300 cc. of water and filtered again to give 4.2 g. of *N*,*N*',*N*''-triphenyl-*N*,*N*',*N*''-trimethyltriaminomethane, m.p. 200–240°. The infrared spectrum of this material was identical with that of an authentic sample. When the volatile solvent was removed from the filtrate there remained two layers, mineral oil and a resinous oil which could not be distilled.

_N_,_N_'-Diphenyl-_N_,_N_'-dimethyldiaminomethoxymethane.—A solution of sodium methoxide was prepared by treating 0.99 g. (0.043 g.-atom) of sodium with 6 cc. of methanol in 30 cc. of 1,2-dimethoxyethane. An additional 50 cc. of 1,2-dimethoxyethane was added followed by 12.5 g. of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate. After stirring 1 hr. the reaction mixture was filtered, volatile solvents removed by distillation and filtered again. The oil was distilled to give 6.3 g. (62%) of *N*,*N*'-diphenyl-*N*,*N*'-dimethyldiaminomethoxymethane, b.p. 143–145° (0.5 mm.), n^{25}D 1.5909.

Anal. Calcd. for $C_{16}H_{20}N_2O$: C, 74.96; H, 7.86; N, 10.93. Found: C, 74.90; H, 7.94; N, 10.80.

_N_,_N_'-Diphenyl-_N_,_N_'-dimethyldiaminoisopropoxymethane.—A solution of sodium isopropoxide in isopropyl alcohol was prepared by treating 0.99 g. (0.043 g.-atom) of sodium with 35 cc. of dry isopropyl alcohol. To this was added 35 cc. of dry 1,2-dimethoxyethane, and 12.5 g. (0.04 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate. After stirring 1 hr. 4.0 g. of salts was filtered off and the filtrate distilled to give 7.7 g. (67%) of *N*,*N*'-diphenyl-*N*,*N*'-dimethyldiaminoisopropoxymethane, b.p. 138–140° (0.25 mm.), n^{25}D 1.5696.

Anal. Calcd. for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85. Found: C, 75.60; H, 8.60; N, 9.84.

_N_,_N_'-Diphenyl-_N_,_N_'-dimethyldiamino-_t_-butoxymethane.—A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by heating under reflux a mixture of 1.71 g. (0.044 mole) of potassium metal and 50 cc. of dry *t*-butyl alcohol. A 12.48-g. (0.04 mole) sample of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate was added and the reaction mixture stirred 2 hr. and then allowed to stand overnight. Filtration to remove 5.2 g. of salts and distillation gave 6.6 g. (55%) of *N*,*N*'-diphenyl-*N*,*N*'dimethyldiamino-*t*-butoxymethane, b.p. 144–146° (0.7 mm.), n^{25}D 1.5609.

Anal. Calcd. for $C_{19}H_{26}N_2O$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.82; H, 9.03; N, 9.13.

_N_,_N_',_N_''-Triphenyl-_N_,_N_',_N_''-trimethyltriaminomethane from _N_,_N_'-Diphenyl-_N_',_N_'-dimethyldiaminomethoxymethane.—A 3.3-g. (0.013 mole) sample of *N*,*N*'-diphenyl-*N*,*N*'-dimethyldiaminomethoxymethane was sealed in a vial and heated on the steam bath for 30 hr. Filtration yielded 0.6 g. (31% based on recovered starting material) of *N*,*N*',*N*''-triphenyl-*N*,*N*',*N*''-trimethyltriaminomethane, identified by its infrared spectrum. Distillation of the filtrate gave 0.9 g. of recovered *N*,*N*'-diphenyl-*N*,*N*'-dimethyldiaminomethoxymethane, b.p. 155–160° (2 mm.).

_N_-Phenyl-_N_-methylaminodithiomethylmethane.—Into a stirred mixture of 0.92 g. (0.04 mole) of sodium and 50 cc. of dry 1,2-dimethoxyethane was condensed 30–40 cc. of methyl mercaptan, dried by passage through 4A molecular sieves and Drierite. A 10-cc. portion of anhydrous methanol was added and, when all the sodium had reacted, 12.5 g. (0.04 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate. After standing overnight the volatile solvent was distilled under vacuum and the precipitated salts (4.4 g.) filtered off and washed with a little 1,2-dimethoxyethane. The filtrate was distilled to give 1.9 g. of *N*-methylaniline, b.p. 40° (0.5 mm.) to 35° (0.25 mm.) and 2.8 g. (30%) of *N*-phenyl-*N*-methylaminodithiomethylmethane, b.p. 110–114° (0.25 mm.). After recrystallization from isoöctane it melted at 47–50°.

Anal. Calcd. for $C_{10}H_{15}NS_2$: C, 56.29; H, 7.09; N, 6.57; S, 30.05. Found: C, 56.49; H, 7.13; N, 6.54; S, 30.08.

_N_,_N_'-Diphenyl-_N_-methylformamidine.—A mixture of 3.72 g. (0.04 mole) of aniline, 1.92 g. (0.04 mole) of a 50% dispersion of sodium hydride in mineral oil and 50 cc. of dry 1,2-dimethoxyethane were heated under reflux for 1 hr. There was now added in small portions 12.5 g. (0.04 mole) of *N*,*N*'-diphenyl-*N*,*N*'-dimethylformamidinium fluoborate. After standing overnight the reaction mixture was filtered and the filtered solid slurried with water and filtered to give 2.25 g. of *N*,*N*',*N*''-triphenyl-*N*,*N*',*N*''-trimethyltriaminomethane, m.p. 225–240° dec. The filtrate from above was distilled to give 2.7 g. of *N*-methylaniline, b.p. 30–40° (0.25 mm.) and 4.4 g. (52%) of *N*,*N*'-diphenyl-*N*-methylformamidine, b.p. 133–147° (0.25 mm.). The infrared spectrum of this material was identical to that of material prepared from *N*,*N*'-diphenylformamidine and methyl iodide.

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(6) J. V. Braun, *Ber.*, **41**, 2147 (1908).

N-Phenyl-N-methyl-N'-ethylformamidine.—To a stirred mixture of 1.92 g. (0.04 mole) of a 50% dispersion of sodium hydride in mineral oil, 15 cc. of ethylamine, and 100 cc. of dry 1,2-dimethoxyethane was added in portions 12.5 g. (0.04 mole) of N,N'-diphenyl-N,N'-dimethylformamidinium fluoborate. An additional 5 cc. of ethylamine was added and the whole allowed to stand overnight. The reaction mixture was filtered to remove 3.7 g. of salts, the volatile solvent distilled under reduced pressure and an additional 1.2 g. of salts filtered off. Distillation gave 2.7 g. (63%) of N-methylaniline, b.p. 40–50 (0.25 mm.) and 2.1 g. of pure N-phenyl-N-methyl-N'-ethylformamidine, b.p. 70–72° (0.25 mm.). The yield including 5.6 g. of the picrate of N-phenyl-N-methyl-N'-ethylformamidine isolated from an intermediate fraction was 67%.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.91; H, 8.98; N, 17.35.

The monopicrate of N-phenyl-N-methyl-N'-ethylformamidine after recrystallization from alcohol melted at 134–136°.

Anal. Calcd. for $C_{16}H_{17}N_5O_7$: C, 49.10; H, 4.38; N, 17.90. Found: C, 49.07; H, 4.53; N, 17.92.

N-Phenyl-N-methyl-N'-n-butylformamidine.—To a stirred mixture of 1.92 g. (0.04 mole) of a 50% dispersion of sodium hydride in mineral oil, 3.0 g. (0.04 mole) of n-butylamine and 100 cc. of dry 1,2-dimethoxyethane was added in portions 12.5 g. (0.04 mole) of N,N'-diphenyl-N,N'-dimethylformamidinium fluoborate. After standing overnight the reaction mixture was filtered to remove 4.8 g. of salts and distilled to give 5.5 g. (72%) of N-phenyl-N-methyl-N'-n-butylformamidine, b.p. 89–96° (0.25 mm.), $n^{25}\text{D}$ 1.5420.

Anal. Calcd. for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.73. Found: C, 75.62; H, 9.83; N, 14.35.

N-Phenyl-N-methyl-N'-benzoylformamidine.—A 4.6-g. (0.038 mole) sample of benzamide was dissolved in 120 cc. of 1,2-dimethoxyethane and 1.75 g. (0.038 mole) of a 53% dispersion of sodium hydride in mineral oil added. The mixture was heated at 80° until hydrogen evolution ceased and then 12.0 g. (0.038 mole) of N,N'-diphenyl-N,N'-dimethylformamidinium fluoborate added. After stirring overnight under nitrogen the reaction mixture was filtered and the filtrate evaporated to dryness in a rotating evaporator to yield a tan semisolid. Crystallization from ether gave 4.2 g. (46%) of N-phenyl-N-methyl-N'-benzoylformamidine, m.p. 62–65°. The filtrate from the crystallization was distilled to give 3.5 g. (85%) of N-methylaniline.

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.08; H, 5.97; N, 11.64.

N,N'-Diphenyl-N,N'-dimethyldiaminotrichloromethylmethane.—A mixture of 21 g. (0.067 mole) of N,N'-diphenyl-N,N'-dimethylformamidinium fluoborate, 12.5 g. (0.067 mole) of sodium trichloroacetate, and 100 cc. of 1,2-dimethoxyethane were stirred for 24 hr. The reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure in a rotating evaporator. The material remaining was extracted with warm benzene and the benzene solution evaporated to dryness in a rotating evaporator to give 17.5 g. (76%) of N,N'-diphenyl-N,N'-dimethyldiaminotrichloromethylmethane, m.p. 78–82°. Recrystallization from petroleum ether (b.p. 30–60°) gave 15.2 g. melting at 82–84°.

Anal. Calcd. for $C_{16}H_{17}N_2Cl_3$: C, 55.91; H,499; N, 8.15; Cl, 30.95. Found: C, 55.32; H, 5.31; N, 8.14; Cl, 31.13.

N,N'-Di-p-Nitrophenyl-N,N'-dimethylformamidinium Fluoborate.—A cold mixture of 18 cc. of concentrated nitric acid and 30 cc. of concentrated sulfuric acid was swirled in an ice bath while 18 g. (0.057 mole) of N,N'-diphenyl-N,N'-dimethylformamidinium fluoborate was added in small portions. The mixture was allowed to warm to room temperature and to stand for 0.5 hr. It was then poured into 200 cc. of ice water containing a little chipped ice. A 200-cc. portion of methylene chloride was added and the mixture swirled until all the oil crystallized. It was then rapidly filtered, washed with methylene chloride, and the wet cake immediately dissolved in 43 cc. of warm 50% fluoboric acid. On cooling in ice there crystallized 14.6 g. (63%) of N,N'-di-p-nitrophenyl-N,N'-dimethylformamidinium fluoborate, m.p. 155–159°. A second crystallization from 50% fluoboric acid gave material melting at 159–162°.

Anal. Calcd. for $C_{15}H_{15}N_4O_4BF_4$: C, 44.80; H, 3.76; N, 13.93. Found: C, 44.73; H, 3.74; N, 14.07.

Hydrolysis of N,N'-Di-p-nitrophenyl-N,N'-dimethylformamidinium Fluoborate.—A mixture of 1.0 g. (0.0024 mole) of N,N'-di-p-nitrophenyl-N,N'-dimethylformamidinium fluoborate, 30 cc. of methylene chloride, and 10 cc. of water was stirred for 48 hr. at room temperature. The layers were separated and the organic layer stripped to dryness on a rotating evaporator and then 3 hr. longer under high vacuum. The remaining solid was crystallized from 200 cc. of carbon tetrachloride to give 0.35 g. (97%) of p-nitro-N-methylaniline, m.p. 140–150°. A second crystallization from carbon tetrachloride gave material melting at 149–151°. (reported[7] 150–151°). The filtrate from the first crystallization was stripped on the rotating evaporator and the crude product crystallized from isopropyl alcohol to give 0.25 g. (58%) of p-nitro-N-methylformanilide, m.p. 110–115°. A third crystallization from isopropyl alcohol gave material melting at 114–117° (reported[8] 118–120°).

N,N'-Di-p-nitrophenyl-N,N'-dimethylformamidinium Fluoborate from N,N',N''-Tri-p-nitrophenyl-N,N',N'',-Trimethyl Triaminomethane.—A 1-g. (0.0021 mole) sample of N,N',N'' - tri - p - nitrophenyl - N,N',N'' - trimethyltriaminomethane was dissolved in 10 cc. of 48% fluoboric acid by gentle warming on the steam bath. The brown solution was cooled in ice for 0.5 hr., filtered, and the precipitate washed with 10 cc. of water and rapidly dried under high vacuum. The yield was 0.5 g. of N,N'-di-p-nitrophenyl-N,N'-dimethylformamidinium fluoborate, m.p. 145–157. After recrystallization from fluoboric acid it melted at 159–161°.

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(7) E. Bamberger, *Ber.*, **27**, 379 (1894).

(8) G. Morgan and W. Grist, *J. Chem. Soc.*, **113**, 690 (1918).