hydrogen (5 hr.). The catalyst was filtered off, the ethanol removed at atmospheric pressure and the residue distilled through a modified Claisen flask with a 25-cm. Vigreux column. The fractions boiling at 80–81° (39 mm.), n_D^{25} 1.4479, weighed 9.0 g. (64% yield). Redistillation yielded 8.2 g. of a colorless liquid, b.p. 80° (38 mm.), n_D^{25} 1.4482.

The infrared spectrum exhibited no absorption bands usually assigned to carbon-carbon unsaturation.

When the preparation was repeated using 1.0 g. of 10% palladium on activated charcoal as the catalyst, a 50% yield was realized.

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92. Found: C, 76.94; H, 13.59; N, 9.63.

The *hydrochloride* had m.p. 137–142°.

Anal. Calcd. for $C_9H_{20}ClN$: C, 60.82; H, 11.34; N, 7.88. Found: C, 60.20; H, 11.03; N, 7.90.

3-Pyrrolidino-3-methyl-1-butene (XXVIII). To 13.7 g. (0.10 mole) of 3-pyrrolidino-3-methyl-1-butyne and 60 ml. of petroleum ether in a thick-walled bottle was added 0.07 g. of 10% palladium on activated charcoal. The mixture was shaken with hydrogen at an initial pressure of 50 *p.s.i.g.* until the pressure drop indicated absorption of 0.1 mole of hydrogen (1 hr.). The catalyst was filtered off, the petroleum ether removed by distillation at atmospheric pressure and the residue distilled through a modified Claisen with a 25-cm. Vigreux column. The fractions boiling between 74–74.5° (36 mm.), n_D^{25} 1.4560–1.4571 were collected; weight 12.8 g. Redistillation gave b.p. 56° at 16 mm., n_D^{25} 1.4571, weight 12.0 g. (86% yield).

The infrared spectrum showed bands at 3.28, 6.14, 7.07, 9.98, 10.99 and 14.55 μ.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31. Found: C, 76.99; H, 12.52.

The *methiodide* had m.p. 152–158° dec.

Anal. Calcd. for $C_{10}H_{20}NI$: N, 4.98. Found: N, 5.00.

3-Dimethylamino-3-methyl-1-butene (XXIX) was prepared by the same procedure with 11.1 g. (0.10 mole) of dimethylamino-3-methyl-1-butyne, 0.065 g. of 10% palladium on activated charcoal and 60 ml. of petroleum ether. The hydrogenation time was 10.5 hr. The fractions boiling between 110–114°, n_D^{25} 1.4225–1.4230 were collected; weight 7.3 g. (63% yield). Redistillation gave material with b.p. 113°, n_D^{25} 1.4231.

Anal. Calcd. for $C_7H_{15}N$: C, 74.27; H, 13.36. Found: C, 74.78; H, 13.06.

The *methiodide* had m.p. 155–158° dec.

Anal. Calcd. for $C_8H_{18}N$: N, 5.49. Found: N, 5.75.

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The Chlorination of *N*,*N*-Dimethylaniline

T. H. CHAO AND L. P. CIPRIANI

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The chlorination of *N*,*N*-dimethylaniline with molecular chlorine gives 2-chloro- and 2,4-dichloro-*N*,*N*-dimethylaniline as the chief products. The chlorination with *N*-chlorosuccinimide, however, yields 39% 4-chloro- and 43% 2-chloro-*N*,*N*-dimethylaniline. This 4-chloro derivative has been found more reactive than the 2-chloro isomer in a competitive reaction with chlorine at about 40°, but the two have been found to react at about the same rate with *N*-chlorosuccinimide in the kinetic studies made.

Chlorination of *N*,*N*-dimethylaniline was reported by Krell[1] in 1872 to give an undefined mixture of monochlorodimethylanilines as well as 2,4-dichloro- and 2,4,6-trichloro-*N*,*N*-dimethylaniline. The nature of the mixture of the monosubstituted products was elucidated by Tishchenko[2] who reported that equal quantities of 2- and 4-chloro-*N*,*N*-dimethylanilines were formed on treatment of a suspension of *N*,*N*-dimethylaniline in aqueous sodium carbonate with chlorine. More recently Danilov and Koz'mina[3] have stated that chlorination with *N*-chloroacetanilide gave rise to both 2- and 4-chloro derivatives while Carpmael[4] found that the use of chlorine gave only 2-chloro-*N*,*N*-dimethylaniline as the monosubstituted product. These results are in marked contrast with the bromination and nitrosation of *N*,*N*-dimethylaniline which give principally the 4-substituted product. The present work was undertaken to investigate the apparent anomaly of this chlorination reaction.

It was found that chlorination of *N*,*N*-dimethylaniline with chlorine in various solvents, sulfuryl chloride in chlorobenzene, dichlorine oxide in carbon tetrachloride, and sodium hypochlorite in acid and basic solutions all gave 2-chloro- and 2,4 dichloro-*N*,*N*-dimethylaniline. The 4-chloro-*N*,*N*-dimethylaniline was found only in small or trace quantities. Chlorination with *N*-chloro reagents such as *N*-chlorosuccinimide, 1,3-dichloro-5,5-di-

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(1) G. Krell, Ber., 5, 878 (1872).

(2) D. V. Tishchenko, *J. der Russ. Phys. Chem. Gessell.*, 60, 161 (1928).

(3) S. N. Danilov and O. P. Koz'mina, *Zhur. Obschei Khim.* (*J. Gen. Chem.*), 19, 309–317 (1949).

(4) W. Carpmael, Br. Pat. 288,665; Ger. Pat. 453,427, Fr. Pat. 634,255.

methyl hydantoin, and hexachloromelamine, on the other hand, definitely gives an appreciable yield of 4-chloro-*N*,*N*-dimethylaniline. The use of *t*-butyl hypochlorite also yields some 4-isomer, but to a lesser extent. Chlorination of dimethylaniline with purified *N*-chlorosuccinimide in dimethylformamide yielded a mixture containing 43% 2-chloro- and 39% 4-chloro isomers; interestingly in this reaction the formation of 2,4-dichlorodimethylaniline was practically nil. In fact, all the data seem to indicate an inverse relationship between the yields of 4-chloro- and 2,4-dichlorodimethylaniline. In the cases where *N*-chloro reagents were used the yield of the 4-chloro derivative was appreciable and the yield of the 2,4-dichloro compound was low. When chlorine was used, the reverse was true. This observation suggested that the 2,4-dichloro compound was formed from the 4-chloro isomer.

In the reaction with *N*-chlorosuccinimide there appeared to be an induction period which is suggestive of a free-radical process. However, the introduction of free-radical initiators such as azobisisobutyronitrile or the use of light failed to affect the reaction as observed or to increase the yield of the 4-chloro isomer when chlorine was used. It is unfortunate that not all the starting *N*,*N*-dimethylaniline could be accounted for in these reactions because of the inevitable accompanying oxidation reactions, but in no case was there any 3-chloro isomer found in the gas-chromatographical analyses.

The chlorination with *N*-chlorosuccinimide is strongly influenced by the reaction medium. In dimethylformamide the reaction gave the best yield of the 4-chloro isomer, while in dimethylformamide with 37% hydrochloric acid, water, or lithium chloride added, the yields approached those obtained with free chlorine as shown in Table II.

An explanation of the difference between the *N*-chlorochlorinating agents and chlorine is suggested by the competitive chlorination of a mixture of the anilines by molecular chlorine at 38° in chlorobenzene. The solution was saturated with gaseous hydrogen chloride in order to approximate the conditions of a normal experiment at halfway mark.

	Starting Mixture, Mole	After Chlorination, Mole[a]
N,*N*-Dimethylaniline	0.11	0.032
2-Chlorodimethylaniline	0.04	0.058
4-Chlorodimethylaniline	0.04	0.012
2,4-Dichlorodimethylaniline	0.00	0.022
Total	0.19	0.124

[a] Chlorine usage = 0.095 moles (one-half of the molecular quantities of the anilines present). Time equals one hour.

As the reaction is attended by considerable oxidation, the system does not lend itself to kinetic study. However, the results of the competitive study indicate that both *N*,*N*-dimethylaniline and its 4-chloro derivative are attacked under the reaction conditions and it would appear reasonable to assume that the low yield of 4-chloro-*N*,*N*-dimethylaniline is due to its ready conversion to the 2,4-dichloro compound. This view is in agreement with the inverse relationship of the yields of these two products already mentioned.

Kinetic studies of the chlorination with *N*-chlorosuccinimide in dimethylformamide further support this view. The reaction was milder and more easily controlled. The rate constants for this reaction are shown in Table I:

TABLE I

REACTION CONSTANTS (L./MOLE/MIN.)

Temp.	*N*,*N*-Dimethylaniline	2-Chloro-	4-Chloro-
0°	5.27×10^{-5}	5.49×10^{-10}	6.84×10^{-13}
25°	4.29×10^{-4}	3.64×10^{-6}	1.13×10^{-7}
50°	3.23×10^{-2}	6.02×10^{-3}	2.92×10^{-3}
75°	4.01×10^{-1}	3.48	17.53

It is interesting to note that with *N*-chlorosuccinimide the reaction rates at temperatures up to and including 50° were higher for *N*,*N*-dimethylaniline and for the 2-chloro derivative. It was under these conditions that an appreciable amount of the 4-chloro-*N*,*N*-dimethylaniline was isolated.

Thus it would appear that it is essential to have a positive chlorine-type reagent for the direct chlorination of *N*,*N*-dimethylaniline to produce any appreciable amount of 4-chloro-*N*,*N*-dimethylaniline. The yield of the 4-chloro isomer is dependent upon the nature of the solvent and upon the temperature. The data are consistent with the notion that molecular chlorine reacts much more rapidly with 4-chloro-*N*,*N*-dimethylaniline than with the 2-chloro isomer, while *N*-chlorosuccinimide reacts with both species at approximately the same rate at about 40°. Consequently the 4-chloro isomer can be obtained by direct chlorination only with the use of positive-chlorine reagents.

EXPERIMENTAL

General procedure. *N*,*N*-Dimethylaniline was dissolved in enough solvent to give a 20% solution which was then brought to the temperature indicated by using external heating or cooling. An equal molar amount of chlorine was slowly bubbled through the solution by means of a dispersion tube. After the chlorine addition, the solution was stirred for the desired length of time after which it was drowned in water and the amine hydrochloride was neutralized with sodium carbonate. The product was then separated from the aqueous layer along with the solvent which was then distilled at atmospheric pressure, and the crude product was then vacuum distilled.

In cases where a positive-chlorine chlorinating agent was used, it was slowly added to the solution of the *N*,*N*-dimethylaniline. As there was no amine hydrochloride formed

TABLE II

CHLORINATION OF ONE MOLE OF N,N-DIMETHYLANILINE (DMA)

Chlorinating Agent, One Mole	Solvent[a]	Material Added	Temp.	Time, Hr.	DMA Recovered Mole	2-Chloro-DMA, Mole	4-Chloro-DMA, Mole	2,4-Dichloro-DMA, Mole
Chlorine	CCl_4	—	−15	6.0	0.485	0.173	0.017	0.132
"	CCl_4	4 g. benzoyl peroxide, light	20–25	7.0	0.487	0.264	0.028	0.104
"	Chlorobenzene	—	10–40	5.0	0.374	0.286	0.036	0.159
"	Chlorobenzene	12.1 g. iodine	10–15	4.0	0.450	0.274	0.011	0.119
"	DMF	—	15–20	4.0	0.538	0.202	0	0.122
"	Pyridine	—	5–10	16.0	0.342	0.258	0.026	0.092
"	Liq. SO_2	—	−10	4.5	0.319	0.290	0.066	0.043
"	20% NaOH	—	10–12	4.0	0.330	0.190	0.050	0.14
"	37% HCl	—	30–50	4.0	0.160	0.470	0	0.117
12% NaOCl	Acetic acid	—	10–40	7.0	0.09	0.13	0	0.24
Cl_2O	CCl_4	—	5–15	6.0	0.505	0.189	0.032	0.012
Pyridinedichloride	CCl_4	—	20	21.0	0.688	0.118	0.015	0.002
SO_2Cl_2	Chlorobenzene	—	10–15	4.5	0.372	0.364	0.034	0.095
Purified N-chlorosuccinimide[b]	DMF	None	40–50	22.0	0	0.43	0.39	0
N-Chlorosuccinimide	DMF	None	65–70	7.5	0.033	0.393	0.309	0.01
N-Chlorosuccinimide	DMF	160 g. H_2O	40–60	5.0	0.033	0.507	0.191	0.02
"	DMF	100 g. LiCl	40–60	5.0	0.068	0.551	0.138	0.044
"	DMF	238 g., 37% Aq HCl	40–60	5.0	0.302	0.45	0.07	0.088
"	CCl_4	None	50–70	20.0	0.10	0.485	0.280	0.021
"	Acetic acid	None	10	20.0	0.035	0.236	0.124	0.01
1,3-Dichloro-5,5-dimethyl hydantoin[c]	CCl_4	None	10–30	20.0	0.10	0.36	0.193	0.01
Hexachloromelamine[d]	CCl_4	None	10–17	20.0	0.08	0.29	0.09	0.01
t-Butyl hypochlorite	CCl_4	None	10–18	7.0	0.29	0.27	0.15	0.11
t-Butyl hypochlorite	CCl_4	[e]	20–40	5.0	0.36	0.248	0.074	0.06
t-Butyl hypochlorite	t-C_4H_9OH	None	20–40	4.0	0.44	0.196	0.047	0.09

[a] DMA in solvent as 20% solution. [b] Recrystallized from water, dried; other N-chlorosuccinimide samples are pure grade materials as supplied by laboratory supply houses, m.p. 147–149°. [c] One-half mole. [d] One-sixth mole. [e] Added 8 g. azobisisobutyronitrile.

when using the N-chlorinating agents or t-butyl hypochlorite, the neutralization with sodium carbonate was omitted.

Method of analysis. The mole figures presented were obtained by vapor phase chromatography of the simply distilled reaction products. In the distillation of the crude products, no attempt was made to separate the isomers, but simply to distill all the volatile matters from the tarry residue. This distilled mixture was then analyzed, and the residue from this distillation is considered in the over-all yield of components. The accuracy of this analytical method, employing vapor phase chromatography, was checked by actual fractionation of several large-scale chlorination reactions. As the boiling points of 4-chloro- and 2,4-dichlorodimethylaniline are practically identical, chlorine analyses were made to determine the proportions of the components in these fractions. In general, good agreements were obtained.

Kinetic studies. The kinetics of the chlorination of N,N-dimethylanilines were studied by a Differential Thermal Analysis apparatus similar to that described by Borchardt and Daniels.[5] Solutions of $0.5M$ N-chlorosuccinimide and $0.5M$ N,N-dimethylaniline in dimethylformamide were allowed to react and dimethylformamide was used as reference material. Second order rate constants were calculated by equations of Borchardt and Daniels.[5] Infrared analyses were made to ascertain that the products were actually chlorinated dimethylanilines.

The gas chromatography instrument used was the Model 124 from F & M Scientific Glassware Company. The separation was achieved by using a 6-ft. Apiezon L column.

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BOUND BROOK, N. J.

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[5] H. J. Borchardt and F. Daniels, *J. Am. Chem. Soc.*, **79**, 41 (1957).