1603

Downloaded by University of Arizona on 08 December 2012 Published on 01 January 1968 on http://pubs.rsc.org | doi:10.1039/J39680001603

Vilsmeier Adducts of Dimethylformamide

By M. D. Scott and H. Spedding,* Esso Research Centre, Esso Petroleum Company, Limited, Abingdon, Berkshire

The reactions of dimethylformamide with cyanogen chloride and with thionyl chloride have been studied, and several of the products identified by spectroscopic methods. As in the case of a previously reported reaction between dimethylformamide and cyanuric chloride, Vilsmeier adducts are formed. For the cyanogen chloride reaction a mechanism is put forward that accounts for the products more satisfactorily than would the cyanuric chloride mechanism. Among the products, those identified are 3-dimethylamino-2-azaprop-2-enylidene-dimethylammonium chloride, 3-(*NV*-dimethylcarbamoyl)-1,1-dimethylformamidine, 1,1-dimethylformamidine, 1,1-dimethylformamidine, 1,1-dimethylformamide. The adduct formed between dimethylformamide and thionyl chloride is fairly stable, but it does decompose slowly in air in a complex manner. Several of the products were identified. The adduct reacts with aniline to form 1,3-diphenylformamidine in addition to the expected 1,1-dimethyl-3-phenylformamidine.

THE adducts formed between amides and non-metallic inorganic halides are well known and are involved as catalysts in a number of reactions of which the bestknown is the Vilsmeier aldehyde synthesis.¹ The structure of the adducts has been the subject of considerable research,² but it is now generally accepted that the most probable structure is (I).

¹ A. Vilsmeier and A. Haack, Ber., 1927, 60, 119.

² H. H. Bosshard and Hch. Zollinger, *Helv. Chim. Acta*, 1959, **42**, 1659.

The thermal stability of the adducts is rather low, and when they are heated, the chloride (II) is formed. Under anhydrous conditions, these chlorides (II) are fairly stable, but they react readily with water and with amines to give the amide and amidines, respectively. The latter reaction is probably the best route to the otherwise rather inaccessible NNN'-trisubstituted amidines.^{3,4}

$$[RR'N^+:CH\cdotO\cdotX \iff RR'N\cdotCH^+:O\cdotX]Cl^- (I)$$

$$(R,R' = Alk, Ar, H; X = SOCl, POCl_2, etc.)$$

$$Me_2N\cdotCHO + SOCl_2 - Me_2N^+:CH\cdotO\cdotSOCl Cl^- \xrightarrow{\Delta}_{-SO_2} Me_2N^+:CHCl Cl^- (II)$$

$$Me_3N^+:CHCl Cl^- + RNH_2 \longrightarrow Me_3N\cdotCH:NR + 2HCl$$

Gold ⁵ has recently reported the reaction of cyanuric chloride with dimethylformamide, and has shown that a di-adduct (III) can be isolated, provided that the reaction temperature is maintained below 10° . If the temperature rises above 10° an unstable tri-adduct is formed which rapidly reacts with 3 mol. of the amide to give 3-dimethylamino-2-azaprop-2-enylidenedimethylammonium chloride (IV) and carbon dioxide. These reactions are shown in the Scheme.



Cyanogen Chloride and Cyanuric Chloride Adducts.— We have studied the reaction between cyanogen chloride and dimethylformamide and have found that, while there are some parallels with the reaction involving cyanuric chloride, the reaction is more complex and may proceed by a different mechanism. When cyanogen chloride was passed into boiling dimethylformamide for $1\frac{1}{2}$ hr., 75% of the amide was recovered unchanged and the other 25% had reacted with cyanogen chloride to form a viscous, water-soluble, brown gum. Chromatographic separation gave the following products (approximate yields based on unrecovered dimethylformamide): 3-dimethylamino-2-azaprop-2-enylidenedimethylammonium chloride (IV), 13%; 3-(NN-dimethylcarb-

$$\begin{array}{ccc} Me_2N \cdot CO \cdot N : CH \cdot NMe_2 & Me_2N \cdot CH : NH_2^+ Cl^- \\ (V) & (VI) \end{array}$$

amoyl)-1,1-dimethylformamidine (V), 17.5%; 1,1-dimethylformamidine hydrochloride (VI), 8%; 1,1-di-

³ E. Beckmann and E. Fellrath, Annalen, 1893, 273, 1.

⁴ J. v. Braun, F. Jostes, and A. Heymons, Ber., 1927, 60, 92.

methylurea (VII), 2%; 1,1-dimethylbiuret (VIII), 10.5%; dimethylamine hydrochloride, 19%; and cyanuric acid 7.5%.

The structure of (IV) was confirmed by a comparison of the infrared spectrum with that published by Gold.⁵ In the ¹H n.m.r. spectrum (measured in deuteriochloroform) the two pairs of geminal N-methyl groups gave signals at τ 6.6 and 6.7, while the two equivalent ·CH: protons occurred at τ 0.7. The structure of the amido-amidine (V) was deduced from the molecular formula obtained by high-resolution mass spectrometry, and confirmed by the infrared and ¹H n.m.r. spectra. The compound was almost certainly present in the protonated form in the crude reaction product, but, owing to the low basicity of (V), chromatography on alumina released the free The ¹H n.m.r. spectrum (measured in water) base. indicates that the structure of the protonated form of the amido-amidine is predominantly Thus, there were three $Me_2N^+:CH^{\bullet}N:C(OH)^{\bullet}NMe_2$. separate N-methyl signals (all singlets), at τ 6.48 (3 H), 6.62 (3H), and 6.90 (6H), as opposed to two in the spectrum of the free base (V), whether the latter was measured in deuteriochloroform or water. This increase denotes that, on one of the terminal nitrogen atoms, the geminal methyl groups have become more dissimilar as a result of a greater degree of double-bond character in the adjacent nitrogen-carbon bond. In addition, the CH:N proton signal was shifted downfield to τ 1.33 from its position (τ 1.77 in aqueous solution) in the spectrum of the free base (V). Moreover, this signal was now a definite multiplet of at least five peaks, with a splitting of approximately 1 c./sec. This multiplet could arise only by a coupling to the protons of the two such coupling was not apparent. The increased coupling is consistent with the postulated increase in the doublebond character of the nitrogen-carbon bond. In aqueous acid solution, the OH proton would be expected to exchange rapidly with the H₂O and H₃O⁺ protons, and no separate signal was expected. Certainly none was present as far downfield as τ 1.7, and the spectrum was not measured beyond that.

The protonated form of the base is not stable in aqueous acid solution. Successive scans of the ¹H n.m.r. spectrum, over a period of several days, indicated the formation of dimethylamine hydrochloride and a compound thought to be the carbamic acid derivative $Me_2N\cdot CH:N\cdot CO_2H$.

1,1-Dimethylformamidine hydrochloride (VI) was identified by the presence of a band in the infrared spectrum at 1715 cm.⁻¹ (a similar frequency to that of the C:N⁺ group in other protonated amidines⁶), and by subsequent comparison (infrared) with an authentic sample. The other products, *viz.*, the urea and biuret derivatives (VII) and (VIII), the dimethylamine hydrochloride, and cyanuric acid, were identified

⁵ H. Gold, Angew. Chem., 1960, 72, 956.

⁶ G. R. Pettit and L. R. Garson, Canad. J. Chem., 1965, 43, 2640.

by comparison of the physical and spectroscopic properties with those of authentic samples.

In the presence of an amine, such as diphenylamine, the reaction appears to be less complex, for when cyanogen chloride was passed into a boiling solution of the amine in dimethylformamide, diphenylformamide was obtained in 41% yield on alkaline work-up. A small quantity (5%) of diphenylcyanamide was also obtained. When cyanuric chloride was substituted for cyanogen chloride, the reaction followed a similar course, but the yield of diphenylformamide was 66%. When the reaction with cyanogen chloride was repeated and the mixture worked up under anhydrous conditions, diphenylformamide was obtained in 79% yield. In addition, however, a small quantity of cyanuric acid (2.8%) and a mixture of salts (20%) were also isolated. The infrared spectrum of the salt mixture suggested that it contained the substituted ammonium chloride (IV), the amidine hydrochloride (VI), and dimethylamine hydrochloride. Under the same conditions, cyanuric chloride yielded the quaternary salt (IX) in addition to a mixture of cyanuric acid and its diphenylamine derivatives. (IX) was identified by the fact that it gave diphenylformamide in high yield on treatment with dilute alkali, and by the ¹H n.m.r. spectrum. The two



methyl groups exhibited a large chemical-shift difference of 1 p.p.m., much larger than in any other of the compounds examined, which is very probably caused by the unequal ring-anisotropy effects of the two phenyl groups. This explanation requires the configuration of the cation to be constrained by the N----CH⁺----N double bonding. A similar effect in N-arylformamidinium salts was accounted for in the same way.⁷

DISCUSSION

The reason that the reaction with cyanogen chloride is apparently more complex than that with cyanuric chloride could be the higher temperature employed in the former reaction. At least two mechanisms can be suggested. The first mechanism would initially involve trimerisation of cyanogen chloride to cyanuric chloride, followed by reaction with dimethylformamide according to the mechanism proposed by Gold.⁵ The main objection to this mechanism is that the products were essentially the same when the experiment was carried out with an excess of xylene as solvent as when the solvent was absent, and yet there was no evidence for the formation of cyanuric chloride when cyanogen chloride alone was passed into boiling xylene. The possibility that trimerisation is catalysed by the presence of dimethylformamide cannot be excluded, but we have not investigated this possibility.

$$\begin{bmatrix} Me_{2}N \cdot \overrightarrow{CH} \cdot OCN & \longleftrightarrow Me_{2}N \cdot \overrightarrow{CH} \cdot OCN \end{bmatrix} Cl^{-} \\ (X) \\ Me_{2}N - \overrightarrow{CH} \\ (X) \\ N \equiv C \\ (X) \\ N \equiv C \\ (X) \\ Me_{2}N \cdot \overrightarrow{CH} \cdot N: CH \cdot NMe_{2} \\ & \vdots \\ Me_{2}N \cdot \overrightarrow{CH} \cdot N: CH \cdot NMe_{2} \\ & \vdots \\ Me_{2}N \cdot \overrightarrow{CH} \cdot N: CH \cdot NMe_{2} \\ & \vdots \\ (IV) \\ (XI) \\ & \vdots \\ (X) \\ & \vdots \\ (X)$$

The second and more probable route, shown in the Scheme, involves the formation from cyanogen chloride and dimethylformamide of a simple adduct (X). Rearrangement of (X) yields the isocyanate (XI) which reacts with a further molecule of dimethylformamide to yield the transitory cyclic intermediate (XII) in a manner similar to the reaction of phenyl isocyanate with dimethylformamide.⁸ (XII) decomposes to give the substituted ammonium chloride (IV) and carbon dioxide.

$$\begin{array}{cc} \mathrm{Me_2N^+:CH \cdot NCO\ Cl^- +\ Me_2NH \longrightarrow} \\ \mathrm{(XI)} & \mathrm{Me_2N \cdot CH : N \cdot C(OH) : NMe_2^+\ Cl^-} \end{array}$$

The formation of the amido-amidine (V) can be explained by the reaction of the isocyanate (XI) with dimethylamine. The origin of the dimethylamine is uncertain, but, since it appeared as the hydrochloride among the products of the reaction, it is not unreasonable to consider it to be an intermediate in the formation of other products.

The most probable origin of 1,1-dimethylurea (VII) is by reaction of dimethylamine with cyanic acid which could be formed by thermal decomposition of the primary adduct (X) (see Scheme). 1,1-Dimethylbiuret (VIII) could arise by reaction of cyanic acid with 1,1-dimethylurea, or by reaction of the dimer of cyanic acid with dimethylamine. The small quantity of cyanuric acid, present among the products, could have originated by trimerisation of the cyanic acid.

$$\begin{array}{c} \text{Me}_{2}\text{N}^{+}:\text{CH}\cdot\text{OCN}\ \text{Cl}^{-} \longrightarrow \text{Me}_{2}\text{N}^{+}:\text{CH}\text{Cl} + \text{HO}\cdot\text{CN} \\ \text{(X)} & & & \\ & &$$

The amidine hydrochloride (VI) could arise from the equilibrium that apparently exists, under certain conditions, between the substituted ammonium chloride

⁷ K. M. Wellman and D. L. Harris, Chem. Comm., 1967, 256.

⁸ M. L. Weiner, J. Org. Chem., 1960, 25, 2245.

(IV) and 1,1-dimethylformamidine. When (IV) was treated at reflux temperature with water or ammonia in dimethylformamide, the amidine hydrochloride (VI) was formed in 40% yield. Conversely, if (VI) was treated with ammonia in chloroform, a basic product was obtained, which, from the ¹H n.m.r. spectrum, consisted of a number of compounds. When this mixture was acidified with picric or hydrochloric acid, a mixture of the substituted ammonium salt (IV) and the 1,1-dimethylformamidine salt was obtained. Similarly, when the preparation of 1,1-dimethylformamidine from dimethylthioformamide and sodamide was carried out, acidification of the crude product yielded the same products.

From these observations it is apparent that a third possibility exists for the mechanism of the formation of the substituted ammonium chloride (IV) in the reaction of cyanogen chloride and dimethylformamide. If 1,1-dimethylformamidine was formed initially by reaction of ammonia with the adduct of dimethylformamide and cyanogen chloride, the substituted ammonium chloride (IV) would be among the observed products. However, when the other observed products are taken into account, the previous mechanism seems more probable.

The mechanism of the formation of diphenylformamide, in the reaction of cyanogen chloride with diphenylamine in the presence of dimethylformamide, undoubtedly involves the reaction of the amine with the primary adduct (X) to give the quaternary salt (IX) which is then readily hydrolysed to diphenylformamide. A similar reaction was observed when diphenylamine was allowed to react with either the adduct of dimethylformamide and thionyl chloride or with the di-adduct (III) of cyanuric chloride and dimethylformamide. The reaction of diphenylamine with cyanogen halides to yield diphenylcyanamide has been reported.9

Thionyl Chloride Adducts .- Bosshard and his coworkers ¹⁰ have described the preparation of the adduct of thionyl chloride and dimethylformamide and its conversion into the amide chloride. We have investigated this reaction and have found that, under the same preparative conditions, the adduct was fairly stable and did not readily evolve sulphur dioxide. On treatment of the adduct with aniline the expected product, 1,1-dimethyl-3-phenylformamidine, was obtained in yields of up to 53%; but, in addition, 1,3-diphenylformamidine was obtained in yields which varied from 10 to 54%. Kühle ¹¹ has reported the same two products from the reaction between dimethylformamide and the amide chloride of formanilide. It is not possible to invoke the same reaction path for the formation of 1,1-dimethyl-3-phenylformamidine from dimethylformamide chloride and aniline as proposed by Kühle for its

⁹ J. v. Braun, *Ber.*, 1900, **33**, 1438.
 ¹⁰ H. H. Bosshard, R. Mory, M. Schmid, and Hch. Zollinger,

Helv. Chim. Acta, 1959, 42, 1653.
 ¹¹ E. Kühle, Angew. Chem., 1962, 74, 861.
 ¹² Yu. V. Mitin, V. R. Glushenkova, and G. P. Vlasov, Zhur. obshchei Khim., 1962, 32, 3867.

formation from formanilide chloride and dimethylformamide. Hence, it seems probable that the 1,3-diphenylformamidine, which appears amongst the products of both reactions, is formed by a subsequent reaction of 1,1-dimethyl-3-phenylformamidine. This suggestion is supported by recent work of Mitin and his co-workers.¹²

The decomposition of the adduct of dimethylformamide and thionyl chloride, when it was exposed to air at room temperature, appears to be quite complex and dependent on length of exposure. Details of the conditions of the reactions and the products identified are in the Experimental section. We have not been able to pursue our study of this system, but hope to present a more detailed report in the future.

EXPERIMENTAL

Alumina was Peter Spence type H. Dimethylformamide was reagent grade, used without further purification. Mass spectra were measured with an A.E.I. MS 9 spectrometer, infrared spectra with a Unicam SP 200 or a Perkin-Elmer Infracord spectrometer, and ¹H n.m.r. spectra with a Varian A-60 spectrometer. In the ¹H n.m.r. spectra tetramethylsilane was used as internal reference except for those measurements on aqueous solutions, where the sodium salt of 2,2-dimethyl-2-silapentane-5-sulphonic acid was used instead, and for the one spectrum measured in perdeuteriodimethyl sulphoxide where the residual ¹H signal was employed.

Reaction of Cyanogen Chloride with Dimethylformamide.-(a) Cyanogen chloride gas was passed into boiling dimethylformamide (190 g.) for $1\frac{1}{2}$ hr., and after the solution had been purged with nitrogen, the excess of dimethylformamide (145 g., 75%) was evaporated under reduced pressure. The residual brown gum (40 g.), which showed strong infrared absorption at 1720 cm.⁻¹, was shaken with chloroform and the mixture filtered. The solid (2.0 g., 7.5%), m.p. $>300^\circ$, was identified as cyanuric acid by comparison of the infrared spectrum with a published spectrum.¹³ The filtrate was evaporated and a sample (15 g.) was chromatographed on alumina (500 g.) to give the following fractions whose yields were estimated from the intensities of the infrared spectra. Fraction 1 (CHCl₃) yielded 3-(NNdimethylcarbamoyl)-1,1-dimethylformamidine (V) (2.9 g., 17.5%) which crystallised as prisms, m.p. 50°, from etherlight petroleum (b.p. 40—60°), molecular formula $C_6H_{13}N_3O$ (mass spectrum), $\nu_{max.}$ (CHCl₃) 1650 (C:O) and 1620 cm.⁻¹ (C:N); n.m.r. (CDCl₃) τ 1.7 (s; CH:N), 6.98 and 7.02 (both s; two CH_3 ·N), with an intensity ratio 1:12 between the CH:N signal and the combined CH₃·N signals; picrate, m.p. $148-151^{\circ}$ (yellow needles from ethanol). Also isolated, 1,1-dimethylurea (VII) (0.4 g., 2%), plates (from benzene), m.p. 179-183° (lit., 14 182°), identical (infrared) with an authentic sample. Fraction 2 (1:1 CHCl₃-MeOH) yielded 1,1-dimethylbiuret (VIII) (1.6 g., 10.5%), plates (from ethanol), m.p. 166-169° (lit., 15 176°), identical (infrared) with an authentic sample. Also, 3-dimethylamino-

¹³ Sadtler Research Laboratories, Inc., Collection of Infrared Standard Spectra, No. 12,499. ¹⁴ T. L. Davis and K. C. Blanchard, J. Amer. Chem. Soc.,

1929, 51, 1790.

¹⁵ D. A. Dunnigan and W. J. Close, J. Amer. Chem. Soc., 1953, 75, 3615.

2-azaprop-2-enylidenedimethylammonium chloride (IV) (0.5 g., 3.3%) was isolated as the picrate, needles (from ethanol), m.p. 135-137° (lit.,⁵ m.p. 137°). Fraction 3 (MeOH) yielded a further quantity (2 g., 10%) of (IV), together with dimethylamine hydrochloride (2 g., 19%), identical (infrared) with an authentic sample; picrate, m.p. 159-161° (lit.,¹⁶ 161°). 1,1-Dimethylformamidine hydrochloride (VI) (2 g., 8%), identical (infrared) with an authentic sample, was also isolated; picrate, m.p. 175-179°.

(b) Cyanogen chloride was passed into a boiling solution of dimethylformamide (50 g.) in dry xylene (200 g.) for $2\frac{1}{2}$ hr. After the solution had been purged with nitrogen, the almost colourless supernatant xylene solution was decanted from the precipitated gum (20.5 g.). The xylene solution was evaporated under reduced pressure, and the residual gum (1.9 g.), on purification, yielded 3-(NN-dimethylcarbamoyl)-1,1-dimethylformamidine (V) (0.24 g., 1.2%), identical (infrared) with the sample obtained in (a). The precipitated gum was chromatographed on alumina (400 g.) and yielded the following products: the substituted ammonium chloride (IV) (8.4 g., 41%), dimethylamine hydrochloride (3.0 g., 14.5%), and 1,1-dimethylformamidine hydrochloride (VI) (4.8 g., 23.5%). The identities of these products were confirmed as in (a).

Decomposition of 3-(NN-Dimethylcarbamoyl)-1,1-dimethylformamidine (V) in Aqueous Hydrochloric Acid.—The ¹H n.m.r. spectra showed that the original signals were replaced by a triplet at τ 7.25, a peak at 6.98, and a singlet at 1.70. The triplet was shown to arise from the Me₂N of dimethylamine hydrochloride, (a) by adding some of that compound and noting the coincidence of the triplet signals, and (b) by repeating the experiment in D₂O-DCl when a single peak, merely broadened by the small H·C·N·D⁺ coupling, appeared in place of the triplet. The positions (τ 6.98 and 1.70) and the intensity ratio (6:1) of the two other signals are consistent with the formation of Me₂N·CH:N·CO₂H, although this compound was not isolated for more definite characterisation. (The CO₂H signal would be merged with the $H_2O-H_3O^+$ peak and was not observed as a separate signal).

Reaction of Cyanogen Chloride with Diphenylamine in Dimethylformamide.-A boiling solution of diphenylamine (50 g.) in dimethylformamide (180 ml.) was treated with cyanogen chloride for $1\frac{1}{2}$ hr. The dark blue mixture was purged with nitrogen. An increase in weight of 13.2 g. was noted. The mixture was then divided into two portions. Portion 1 (138.1 g., 59%) was poured into 5% sodium hydroxide solution (500 ml.) and the mixture extracted with ether. The extract, after being washed with water and evaporated, yielded a brown oil (27.3 g.) which was chromatographed (3 g. of product on 90 g. alumina). The composition of the crude product, estimated from the chromatographic data, was as follows: diphenylamine (21.3 g., 42%), plates, m.p. 53°, identical (infrared) with an authentic sample; NN-diphenylformamide (13.7 g., 41%), prisms (ether-light petroleum), m.p. 65° (lit.,¹⁶ $73-74^{\circ}$), identified by comparison of the infrared spectrum with a published spectrum; 17 and diphenylcyanamide (1.52 g., 5%), infrared spectrum almost identical with that of a sample prepared by the method of Kurzer.¹⁸ Portion 2 (95.1 g., 41%) was evaporated under reduced

pressure and the residual blue gum (54.7 g.) dissolved in chloroform. Cyanuric acid (1.9 g., 2.8%), m.p. >315°, was collected. The filtrate was filtered through Florisil and evaporated, and the residue (36.2 g.) chromatographed on alumina (500 g.). Two fractions were eluted: the first (22.9 g., eluted with chloroform) was shown (g.l.c.) to contain diphenylamine (10.2 g., 50%), NN-diphenylformamide (9.2 g., 79%), and a small quantity of diphenylcyanamide (ν_{max} 2200 cm.⁻¹, C:N); the second (6.75 g., eluted with methanol) appeared from the infrared spectrum to consist of ionic material (broad band 3500-2400 cm.-1) containing the substituted ammonium chloride (IV), the amidine hydrochloride (VI), and dimethylamine hydrochloride.

Reaction of Cyanuric Chloride with Diphenylamine in Dimethylformamide.—(a) A slurry of cyanuric chloride (18.4 g.) in a solution of diphenylamine (50.7 g.) in dimethylformamide (180 ml.) was stirred at room temperature until the initial reaction had subsided. The mixture was refluxed for a further 1 hr., allowed to cool, and then filtered to remove a quantity (2.0 g., 15.5%) of white solid, m.p. 309-311°. This solid, by comparison of the infrared spectrum with that of an authentic sample, appeared to consist mainly of cyanuric acid. The filtrate was poured into water, and the mixture was extracted with ether and washed with water. On evaporation, the extract yielded diphenylamine (4.8 g., 9.5%), m.p. 53°. The aqueous solution was basified with dilute sodium hydroxide solution and again extracted with ether. The extract yielded NN-diphenylformamide (35 g., 66%), plates (from ether), m.p. 75° (lit., 16 73-74°).

(b) The method and quantities used were as described in (a). After the reaction was complete the excess of dimethylformamide (140 ml.) was evaporated under reduced pressure. The residual viscous green gum was treated with ethanol to give a deep-blue solution and an insoluble white solid (12.5 g., 97%), m.p. 309-311°. The solid, by comparison of the infrared spectrum with that of an authentic sample of cyanuric acid, was shown to contain the latter and at least two other high-melting $(>300^\circ)$ unidentified products. The filtrate was evaporated, and the blue gum (70 g.) triturated with acetone to yield the salt (IX) (30 g., 39%), hygroscopic crystals, m.p. 165-170°. The structure assigned (see earlier) is in accord with the n.m.r. spectrum (deuteriochloroform): $\tau 0.75$ (1H; CH:N), 2.30 (10H; two C_8H_5), 6.16 and 7.20 (3H each; two CH_3 .N). The remaining gum (38.5 g.) was dissolved in water and the solution extracted with ether to give diphenylamine (7.3 g.)14%), m.p. 53°. The aqueous solution was basified with dilute sodium hydroxide solution and the precipitated NN-diphenylformamide (13.2 g., 26%) crystallised from ether as plates, m.p. 65°.

Partial Hydrolysis of 3-Dimethylamino-2-azaprop-2-enylidenedimethylammonium Chloride (IV).-A solution of (IV) (20 g.), prepared by the method of Gold,⁵ in dimethylformamide (40 ml.), containing water (2.5 g.), was refluxed for 1 hr. The solution was allowed to stand overnight, when 1,1-dimethylformamidine hydrochloride (VI) (5.2 g., 39%) crystallised as long needles, m.p. 180-182° (lit.,¹⁹ prisms, m.p. 168–169°), v_{max} 1715 cm.⁻¹ (C:N⁺). The reason for the 12° difference in m.p. was not investigated, but may be due to the fact that different crystalline forms

¹⁷ Sadtler Research Laboratories, Inc., Collection of Infrared Standard Spectra, No. 1,989.

- ¹⁸ F. Kurzer, J. Chem. Soc., 1949, 3033.
 ¹⁹ A. Pinner, Ber., 1883, 16, 1643.

were produced by the two preparative methods. The picrate crystallised from ethanol as needles, m.p. 175–178° (Found: C, 36.3; H, 3.7; N, 22.3. Calc. for $C_9H_{11}N_5O_7$: C, 35.9; H, 3.7; N, 23.2%). The filtrate was evaporated to yield unreacted starting material (IV) (12 g., 60%); picrate m.p. 135–137° (lit., ⁵ 137°).

Reaction of 1,1-Dimethylformamidine Hydrochloride (VI) with Anhydrous Ammonia.—A solution of (VI) (1.1 g.) in alcohol-free chloroform (50 ml.) was treated with anhydrous ammonia until precipitation of ammonium chloride (0.5 g., 92.5%) was complete. The excess of ammonia was removed in a stream of nitrogen. The infrared spectrum showed no absorption at 1715 cm.⁻¹ (C:N⁺). Evaporation of the chloroform yielded a red oil (0.6 g., 83%) with a strong ammoniacal odour. The oil appeared from the ¹H n.m.r. spectrum to be a mixture of basic products. Reaction of the oil with an excess of picric acid gave: 1,1-dimethylformamidine picrate, m.p. 175-178°, identical (infrared) with an authentic sample; 3-dimethylamino-2-azaprop-2-enylidenedimethylammonium picrate, m.p. 135-137°, identical (mixed m.p.) with an authentic sample; and an unidentified picrate, m.p. 278-280° (Found: C, 25.3; H, 0.57; N, 14.6%).

Preparation of 1,1-Dimethylformamidine.—A solution of dimethylthioformamide²⁰ (25 g.) in dry toluene (50 ml.) was added dropwise during $\frac{1}{2}$ hr. to a well-stirred suspension of sodamide (25 g.) in boiling toluene (200 ml.). A vigorous reaction occurred accompanied by evolution of white fumes. After the addition was complete, the mixture was heated for a further $\frac{1}{4}$ hr. and then filtered. The solid product (31 g.) appeared from the analytical data to be mainly sodium sulphide containing either a little sodamide or sodium salt of the formamidine (Found: N, 4.7; Na, 48.3; S, 19.36%). G.l.c. of the filtrate indicated that the mixture contained 50% of unreacted dimethylthioformamide and 50% of a very polar compound which was not identified. Reaction with picric acid gave 1,1-dimethylformamidine picrate, m.p. 173°, identical (infrared) with an authentic sample. The toluene solution was saturated with hydrogen chloride and the crude hydrochloride (15 g., 50%) was chromatographed on alumina to give 3-dimethylamino-2-azaprop-2-envlidenedimethylammonium chloride (IV) (2.6 g., 11%; picrate, m.p. 135-137°), and 1,1-dimethylformamidine hydrochloride (VI) (9.0 g., 30%; picrate, m.p. 177-180°); n.m.r. spectrum (perdeuteriodimethyl sulphoxide) of the hydrochloride: $\tau 0.6$ (broad s; approx. 1.5H, $^+NH_2$; removed by D_2O), 2.0 (s; 1H; CH:N), 6.8 and 7.0 (both s; 3H each; two Me.N).

Reaction of Dimethylformamide with Thionyl Chloride.— Ice-cold samples of thionyl chloride (119 g.) and dimethylformamide (73 g.) were mixed, and the mixture was allowed to stand at room temperature for 2 hr. After being heated under reduced pressure on an oil-bath at $50-60^{\circ}$ for a further 2 hr., the adduct was obtained as a crystalline very hygroscopic cake.

Reaction of the Thionyl Chloride-Dimethylformamide Adduct with Aniline.—(a) A solution of aniline (2.8 g.) in chloroform (10 ml.) was mixed with a solution of the adduct (2 g.) in chloroform (10 ml.), and the precipitated aniline hydrochloride (1.0 g., 26%) was collected. The filtrate was evaporated and the crude product (4.2 g.) was dissolved in water and basified with cold dilute sodium hydroxide solution, to yield 1,3-diphenylformamidine (1.58 g., 54%), needles [from ether-light petroleum (b.p. 40-60°)], m.p. 135-138° (lit.,²¹ 135°). The picrate separated from alcohol as needles, m.p. 190-192° (lit.,¹⁶ 193°).

(b) A fresh sample of the adduct was prepared from thionyl chloride (11.9 g.) and dimethylformamide (7.3 g.) and dissolved in chloroform. The solution was cooled, treated with aniline (18.6 g.), and filtered to remove the precipitated aniline hydrochloride (8.7 g., 33.5%). After the chloroform had been evaporated, the crude product (22.6 g)was triturated with acetone to give 1,1-dimethyl-3-phenylformamidine hydrochloride (11.5 g., 62%) as a brown solid, m.p. 195—200°, v_{max} 1690 cm.⁻¹ (C.N⁺). The hydrochloride (10 g.) was treated with dilute sodium hydroxide solution, and on extraction with ether gave a pale yellow oil (7.12 g.). This oil deposited 1,3-diphenylformamidine (0.8 g., 10%) which crystallised from petroleum as needles, m.p. 135-137°. The remaining oil, on distillation gave 1,1-dimethyl-3-phenylformamidine (4.2 g., 53%) as a colourless oil, b.p. 96-97°/1 mm. (lit., 8 68-71°/0.05 mm.); picrate, m.p. 155-158°.

Reaction of Thionyl Chloride-Dimethylformamide Adduct with Diphenylamine.—A solution of diphenylamine in chloroform was added dropwise to a solution of the adduct in the same solvent until reaction was complete. The solution was filtered and evaporated, and the resulting green oil was dissolved in water and extracted with ether to remove the unreacted diphenylamine. The aqueous solution, on basification with sodium hydroxide solution and extraction with ether, yielded 1,1-diphenylformamide, m.p. 65°, identical (infrared) with an authentic sample.

Decomposition of Thionyl Chloride-Dimethylformamide Adduct.—(a) A sample of the adduct was prepared from thionyl chloride (24.6 g.) and dimethylformamide (14.3 g.) and was allowed to stand in contact with the atmosphere for 2 days. The resulting liquid was distilled, to yield dimethylformamide hydrochloride (5 g., 23%), b.p. 55°/10 mm. (lit.,²² 76°/40 mm.), identified by analysis and by comparison of the ¹H n.m.r. spectrum with published data; ²³ n.m.r. spectrum (deuteriochloroform): $\tau - 5.4$ (s; 1H; OH, absent in D₂O solution), 1.35 (s; 1H; :CH·), and 6.6, 6.8 (both s; 3H each; two CH₃·N).

(b) The adduct was prepared as in (a) and exposed to the air for 1 week, by which time the colourless liquid had deposited yellow crystals. The supernatant liquid was shown (infrared) to be a mixture of dimethylcarbamoyl chloride and dimethylformamide hydrochloride. Distillation yielded dimethylcarbamoyl chloride (7.3 g., 35%), b.p. 60°/10 mm., identical (infrared) with an authentic sample. The residue from distillation yielded dimethylformamide hydrochloride (7 g., 32%). The crystalline solid was washed with ether, to give a yellow granular fuming solid (7 g.). The ether washings yielded a further quantity (2.5 g., 12%) of dimethylcarbamoyl chloride. A small quantity of the yellow solid, on trituration with acetone, yielded dimethylamine hydrochloride as needles; picrate, m.p. 155-159° (lit.,¹⁶ 161°). A suspension of the yellow solid (1.28 g.) in ether was treated with an ethereal solution of aniline (1.8 g.). The precipitate, after being washed with water, yielded aniline hydrochloride and 1,1,6,6-tetramethylthiuram disulphide

1608

²⁰ R. Willstätter and T. Wirth, Ber., 1909, 42, 1908.

²¹ P. Oxley, D. A. Peak, and W. F. Short, J. Chem. Soc., 1948, 1618.

²² M. Halmos and T. Mohácsi, Acta Phys. et. Chem. Szeged., 1960, **6**, 99.

³³ S. J. Kuhn and J. S. McIntyre, Canad. J. Chem., 1965, 43, 995.

which crystallised from a mixture of benzene and light petroleum as prisms, m.p. 152-154° (lit.,²⁴ 146°).

(c) On another occasion, a sample of the yellow solid, which had been obtained by accidentally exposing the

²⁴ A. D. Cummings and H. E. Simmons, Ind. Eng. Chem., 1928, **20**, 1173.

primary adduct to air, reacted with aniline to yield dimethylcarbamoyldimethylthiocarbamoyl disulphide, Me_2N ·CO·S·S·CS·NMe₂.

We thank Dr. J. P. Nice for the mass spectrum determination and interpretation.

[8/032 Received, January 8th, 1968]