residue was dissolved in 8 ml. of methyl alcohol and then neutralized with 1.38 g. (0.023 mole) of acetic acid. Gas phase chromatographic analysis showed a formamide content of 0.27 g. (26%). Under the conditions of analysis isobutyramide could not be distinguished from VI.[13] Infrared analysis of the gas in the buret system indicated a trace (<1%) of carbon monoxide; no other gas was observed.

Treatment of N-Methyl-N-isobutyrylformamide (VII) with Sodium Methoxide.—Treatment of VII with sodium methoxide was conducted as described for VI. From 2.83 g. (0.021 mole) of VII and 1.11 g. (0.021 mole) of sodium methoxide were obtained 0.04 g. (4%) of methyl formate, 0.24 g. (36%) of methyl alcohol, and 0.43 g. (20%) of methyl isobutyrate. The yield of N-methylformamide amounted to 24%. N-Methylisobutyramide and VII had the same retention time with the g.p.c. column used for analysis.[13] It was observed that gas evolution began immediately upon mixing the reactants. Infrared analysis showed the gas to be solely carbon monoxide. The total amount of carbon monoxide evolved was 207 ml. (40%).

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Chemistry of Imidoyl and Amide Chlorides. II.[1] On the Preparation and Properties of the N-Mono- and N,N-Dialkyl-Substituted Amide Halides[2,3]

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From a number of N-alkylimidoyl chlorides and HCl, HBr, DCl, and DBr, a series of N-monoalkylamide halides (N-alkylimidoyl chloride hydro or deuterio halides) was prepared. This is the first instance of the preparation and description of this type of compound. Certain new N,N-dialkyl-substituted amide chlorides were prepared from the corresponding N,N-disubstituted 2-furamides with $COCl_2$, or, in less pure form, with PCl_5. The amide chlorides were identified also as N,N'-disubstituted or N,N,N'-trisubstituted amidines by reaction with the corresponding primary amines. On the basis of infrared spectra and other properties the amide chlorides appear to have an immonium salt structure.

By the reaction of N-ethyl-2-furamide with phosphorus pentachloride Wallach[5] prepared a very hygroscopic product, analysis of which approximated that required for the amide chloride, $C_4H_3O\cdot CCl_2NHC_2H_5$. The compound, however, was not further characterized. From N-phenylbenzimidoyl chloride and hydrogen iodide Lander and Laws[6] obtained a mixed amide halide and suggested a covalent structure, $C_6H_5CClINHC_6H_5$. Subsequently, a number of contradicting structure assignments have been reported. In accord with Stephen's[7] results N-phenylbenzimidoyl chloride reacted with 2 moles of hydrogen chloride to give a covalent amide chloride salt, $[C_6H_5CCl_2NH_2C_6H_5]^+Cl^-$, whereas Bosshard and Zollinger[8] suggested an immonium chloride hydrochloride structure, $[C_6H_5C(Cl){=}NHC_6H_5]^+HCl_2^-$ for this compound. Klages[9] reported that the addition of 2 moles of hydrogen bromide to N-methylbenzimidoyl chloride gave an "imidoyl chloride hydrobromide," while the addition of 3 moles of hydrogen chloride produced an "imidoyl chloride sesquihydrochloride." The structures of the compounds, however, were not specified. To the addition products of hydrogen halides with nitriles, in the presence of a metal salt, Meerwein[10] assigned an immonium salt structure, $[RC(Cl){=}NH_2]^+(MeCl_{n+1})^-$. This is in contrast to the nitrilium salt structure assigned to similar compounds by Hantzsch.[11]

Owing to the growing interest in amide chlorides and related compounds,[12] we have examined the addition reaction of hydrogen and deuterium halides to N-alkyl- and N-aryl-2-furimidoyl chlorides. From our data, in contrast to the previous reports,[7-11] the N-alkylamide halides appear to be the only stable addition products. Under the same conditions, N-aryl-2-furimidoyl chlorides reacted with hydrogen chloride to give products which were crystalline but spontaneously dissociated at room temperature and atmospheric pressure.

As we have found earlier,[1] N-aryl-2-furamides react with phosphorus pentachloride with the evolution of hydrogen chloride to form N-aryl-2-furimidoyl chlorides. However, N-methyl-, N-ethyl-, and N-isopropyl-2-furamides reacted with the formation of the corresponding amide chloride as crystalline solids sensitive to moisture but stable in a dry atmosphere. We found the amide chlorides to be practically insoluble in nonpolar solvents and were unable to prepare analytically pure samples by this method, except in the case of compound I, which could be purified by vacuum sublimation, and proved to be identical with the amide chloride prepared by the hydrogen chloride procedure.

In a sealed capillary tube, under nitrogen, the prepared amide halides were observed to melt sharply without decomposition. The ease of addition of hydrogen halides to the N-alkyl-2-furimidoyl chlorides, and the fact that the derived amide halides were insoluble in nonpolar solvents and were easily dehydro-

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[1] Part I: V. Hahn and M. Grdinić, to be published.

[2] Studies in the Furan Series. X. Part IX: see ref. 1.

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halogenated with pyridine or in refluxing benzene,[1] indicated that in our case the amide halides I–IX were of an ionic character. The examination of their infrared spectra showed the characteristic $>C{=}\overset{+}{N}<$ absorption in the region of 6 μ (Table I), as was observed for similar chromophores by Witkop and Patrick,[13] Leonard and Gash,[14] Bosshard and Zollinger,[8] and Arnold and Holly.[15] This indicated that the amide halides I–IX had an immonium salt structure, $[ArC(Cl){=}NHR]^+X^-$ (X = Cl, Br).

In order to locate the position of the N–H band, we measured the spectra of the corresponding N–D compounds (III, IV, and IX), but were unable to make assignments for the N–H or N–D absorptions. This might be attributed to the low intensity of the N–D band or masking by other bands. The broad absorption bands in the region of 3.5–5.5 μ support the proposal of an ionic structure, as these could be attributed to the hydrogen bonding between the N–H proton and the halogen ion. Similar bands were observed by Witkop[13,16] for the hydrochlorides of Schiff bases.

The amide halides I–IX were also identified by conversion to the corresponding N,N′-disubstituted amidines by reaction with aniline.

A considerable effort has been made in the past by many investigators to isolate in a pure state and characterize the amide chlorides derived from N,N-disubstituted amides.[12] Although they were not isolated as such, amide chlorides were suggested as intermediates in some syntheses.[12,17,18] However, some authors expressed their doubts concerning the existence of stable or isolable amide chlorides.[19,20]

It was only recently that the preparation and characterization of several amide chlorides, derived from N,N-disubstituted amides of formic, acetic, and benzoic acid, were reported.[8,21] Bosshard and Zollinger proposed an immonium salt structure,[8] contrary to the then generally accepted covalent formulation, as suggested by von Braun.[12b] Recently Smith[22] and Fawcett[23] reported the preparation of amide fluorides. It is interesting, however, that the n.m.r. spectra and volatility of Fawcett's compounds, *e.g.*, $HCF_2N(CCl_3)_2$ and $C_6H_5CF_2N(CCl_3)_2$, indicate a purely covalent structure.

In this paper we describe the preparation of several N,N-dialkyl-substituted amide chlorides (X–XII). From N,N-dimethyl- and N,N-diethyl-2-furamide and N,N-dimethylbenzamide with phosphorus pentachloride we were able to prepare only impure amide chlorides. They were identified by conversion to N,N,N′-trisubstituted amidines and the corresponding picrates. Pure amide chlorides X–XII (Table I) were prepared from N,N-disubstituted amides and liquid phosgene, by reaction in a sealed ampoule. These products are, like imidoyl chloride hydrohalides, white crystalline substances of relatively high melting points, insoluble in nonpolar solvents and stable in a dry atmosphere. Their infrared spectra showed the strong absorption bands of $>C{=}\overset{+}{N}<$ in the region of 6 μ,[8,13,15] which were consistent with the infrared spectra of imidoyl chloride hydrohalides I–IX and indicated an immonium salt structure, $[ArC(Cl){=}NR_2]^+Cl^-$. The broad hydrogen-bonding band in the region of 2.80–6.00 μ was absent.

N-Methyl-N-phenyl-, N-ethyl-N-phenyl- and N,N-diphenyl-2-furamide failed to react with phosgene even after prolonged heating at 100° in a sealed ampoule.

Experimental[24]

Imidoyl chloride hydro or deuterio halides I–IX were prepared by the following general procedure. Pure, freshly distilled imidoyl chloride was dissolved in 15–80 vol. of petroleum ether (b.p. 60–80°) and a stream of hydrogen halide or deuterium halide, diluted with a tenfold volume of nitrogen, was bubbled in. An immediate precipitation occurred. The suspension was transferred to a drybox, purified by three to five washings and decantations with petroleum ether, and dried.

N,N-Dialkyl-substituted amide chlorides X–XII were prepared in an impure form by the phosphorus pentachloride procedure and identified as N,N,N′-trisubstituted amidines, using von Braun's procedure.[17] Pure samples were prepared from the amide and phosgene by the following general procedure. The freshly distilled amide was placed in a precooled ampoule at −70° and a 350–550% molar excess of liquid phosgene was introduced. The ampoule was sealed and, when allowed to reach room temperature, a vigorous effervescent reaction took place, with simultaneous separation of a crystalline product. After completion of the reaction (1 hr.) the ampoule was cooled to −70°, opened, evacuated, refilled with dry nitrogen, and transferred to a drybox. The product obtained in this way was analytically pure and was further characterized as the N,N,N′-trisubstituted amidine by suspension in dry benzene and treatment with a 300% molar excess of aniline in benzene. The amidines and the picrates were found to be identical with the products obtained by treating impure amide chlorides (prepared by the PCl_5 procedure) with aniline.

N-Methyl-2-furimidoyl Chloride Hydrochloride (I). Phosphorus Pentachloride Procedure.—A mixture of 11.7 g. (0.094 mole) of N-methyl-2-furamide and 19.5 g. (0.094 mole) of phosphorus pentachloride was heated for 30 min. at 100°. After removal of the $POCl_3$, the remaining yellowish crystalline mass was transferred to a sublimation apparatus. Cautious heating at 0.02 mm. resulted in a sublimation of a white crystalline product, m.p. 103–104°. The mixture melting point of the sublimate and the product from N-methyl-2-furimidoyl chloride and hydrogen chloride was undepressed.

Anal. Calcd. for $C_6H_7Cl_2NO$: Cl, 39.39. Found: Cl, 39.48.

N-Methyl-N′-phenyl-2-furamidine.[1]—The amidine, m.p. 99°, was prepared from N-methyl-2-furimidoyl chloride hydrochloride (I) and aniline. The mixture melting point with the amidine prepared from the N-methyl-2-furimidoyl chloride and aniline was undepressed.

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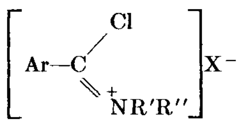
(24) Melting points are uncorrected. The melting points of amide chlorides were measured in sealed capillary tubes under nitrogen. Unless stated otherwise, the samples were dried for 2–12 hr. at 0.01–0.1 mm. over phosphorus pentoxide at room temperature. The N-monosubstituted amides and imidoyl chlorides were prepared as described previously.[1] The N,N-disubstituted amides were prepared from acyl chlorides and the corresponding secondary amines in pyridine. Deuterium chloride and deuterium bromide were prepared from heavy water (99.7%) and phosphorus halides. All manipulations of amide chlorides were performed in a drybox. Infrared spectra were measured on a Model 21 Perkin-Elmer spectrophotometer using sodium chloride plates.

TABLE I

N-MONO- AND N,N-DIALKYL-SUBSTITUTED AMIDE HALIDES



Compd.	Ar	R'	R''	X−	Yield; %	M.p.; °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % Br + Cl	Found, % C	Found, % H	Found, % Br + Cl	Infrared bands, μ $>\overset{+}{C=N}<$	Infrared bands, μ H or D bond	Amidine m.p., °C.
I	2-C_4H_3O	CH_3	H	Cl^-	83	103–104	$C_6H_7Cl_2NO$			39.39			39.23	6.16[a]	3.60–5.28 5.28–5.84	99[b]
II	2-C_4H_3O	CH_3	H	Br^-	93	132–134 dec.	$C_6H_7BrClNO$	32.07	3.15	51.39	31.76	3.04	50.02	6.14[a]	3.60–5.3 5.76	99–100[b]
III	2-C_4H_3O	CH_3	D	Cl^-	97	103–105	$C_6H_6DCl_2NO$			39.18			39.34	6.14[a]	3.55–4.77 4.77–5.75	99–100[b]
IV	2-C_4H_3O	CH_3	D	Br^-	95	133–134 dec.	$C_6H_6DBrClNO$			51.16			51.32	6.12[c]	3.62–4.58 4.58–6.00	99–100[b]
V	2-C_4H_3O	C_2H_5	H	Cl^-	100	93–94	$C_7H_9Cl_2NO$			36.54			36.30[d]			80–81[b]
VI	2-C_4H_3O	C_2H_5	H	Br^-	70	151–152	$C_7H_9BrClNO$			48.37			48.00			80–81[b]
VII[e]	C_6H_5	CH_3	H	Cl^-	96	93–95	$C_8H_9Cl_2N$			37.31			37.28[d]			134–135[e]
VIII[e]	C_6H_5	CH_3	H	Br^-	86	115–117 dec.	C_8H_9BrClN			49.19			48.64	6.18[a]	3.66–5.40 5.61	134–135[e]
IX[e]	C_6H_5	CH_3	D	Br^-	92	115–118 dec.	$C_8H_8DBrClN$			48.98			47.38	6.11[c]	2.90–4.56 4.56–5.80	134–135[e]
X	2-C_4H_3O	CH_3	CH_3	Cl^-	97	181–182 dec.	$C_7H_9Cl_2NO$	43.32	4.67	36.54	43.65	4.77	36.75	6.17[a]	. . .	*f*
XI	2-C_4H_3O	C_2H_5	C_2H_5	Cl^-	93	99–103	$C_9H_{13}Cl_2NO$			31.93			31.74	6.17[a]	. . .	*f*
XII[g]	C_6H_5	CH_3	CH_3	Cl^-	97	124–125[h]	$C_9H_{11}Cl_2N$			34.74			34.84	6.09[a,i]	. . .	73–74 (picrate m.p. 131–132[j])

[a] The infrared spectra were determined from samples suspended in Nujol. [b] See ref. 1. [c] The infrared spectra were determined from samples suspended in hexachlorobutadiene. [d] The samples were dried at atmospheric pressure in a stream of nitrogen for 3 hr. [e] For the preparation of N-methylbenzimidoyl chloride and N-methyl-N'-phenylbenzamidine, see H. Pechmann, *Chem. Ber.*, **28**, 2362 (1895). [f] See Experimental. [g] See ref. 8, 27. [h] Lit. m.p. 95°,[8] 36°.[27] [i] See ref. 8, 6.12 μ. [j] Lit. m.p. 126° (see footnote *e*).

N-Methyl-2-furimidoyl Chloride Hydrochloride (I). Hydrogen Chloride Procedure.—A solution of 2.5 g. (0.017 mole) of N-methyl-2-furimidoyl chloride in 40 ml. of petroleum ether was subjected to a stream of hydrogen chloride, diluted with nitrogen. The product, 2.6 g., was dried for analysis at 0.02 mm. for 2 hr.

With aniline I gave the corresponding **amidine**, which was identical by mixture melting point with the product obtained from N-methyl-2-furimidoyl chloride and aniline.

The other members (II–IX) were prepared in the same way, and the structures were verified by preparation of the amidines and determination of mixture melting points with the amidines prepared from the corresponding imidoyl chlorides (see Table I).

N-Methyl-2-furimidoyl Chloride Methochloride (X).—A mixture of 1.7 g. (0.012 mole) of N,N-dimethyl-2-furamide[25] and 4.0 g. (0.040 mole) of liquid phosgene in a sealed ampoule was treated as described in the general procedure. The product, 2.3 g., was a white crystalline powder. For analysis the compound was dried at 0.01 mm. for 4 hr.

N,N-Dimethyl-N′-phenyl-2-furamidine.—A suspension of X (1.6 g., 0.0084 mole) in 20 ml. of benzene was treated with a solution of 3.0 g. (0.0322 mole) of aniline in 10 ml. of benzene. The amidine (0.9 g., 52%) was a yellow viscous oil, b.p. 159–165° at 14 mm. The product was identified as its picrate, m.p. 122–123°. A mixture melting point with the picrate prepared from the methochloride, obtained by the phosphorus pentachloride procedure, was undepressed.

N,N-Dimethyl-N′-ethyl-2-furamidine was prepared from X and ethylamine, b.p. 95–99° at 12 mm.

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.48. Found: C, 65.12; H, 8.56.

A **picrate** was prepared from the amidine and picric acid. An analytical sample was obtained by recrystallization from aqueous ethanol, m.p. 106–109°.

Anal. Calcd. for $C_{15}H_{17}N_5O_8$: C, 45.57; H, 4.33; N, 17.72. Found: C, 45.83; H, 4.46; N, 17.83.

N-Ethyl-2-furimidoyl Chloride Ethochloride (XI).—A mixture of 1.3 g. (0.0078 mole) of N,N-diethyl-2-furamide[26] and 4.2 g. (0.043 mole) of liquid phosgene was treated as described in the general procedure. The product, 1.6 g., was a white crystalline solid. The sample was dried for analysis at 0.1 mm. for 4 hr.

N,N-Diethyl-N′-phenyl-2-furamidine.—A suspension of XI (2.5 g., 0.0113 mole) in benzene was treated with a solution of 4.2 g. (0.0451 mole) of aniline in 10 ml. of benzene. The amidine, 1.2 g. (44%), was a yellow viscous oil, b.p. 167–168° at 12 mm. The product was purified for analysis by fractional distillation.

Anal. Calcd. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49. Found: C, 74.25; H, 7.42.

The **picrate** was recrystallized from aqueous ethanol; m.p. 83–84°.

Anal. Calcd. for $C_{21}H_{21}N_5O_8$: C, 53.50; H, 4.49; N, 14.86. Found: C, 53.70; H, 4.60; N, 15.01.

N-Methylbenzimidoyl Chloride Methochloride (XII).[8,27]—A mixture of 1.2 g. (0.00804 mole) of N,N-dimethylbenzamide and 4.2 g. (0.043 mole) of liquid phosgene gave 1.6 g. of a white crystalline product, which was dried for analysis at 0.1 mm. for 7 hr. and melted in a sealed capillary tube under nitrogen at 124–125° (see Table I).

N,N-Dimethyl-N′-phenylbenzamidine was prepared from XII and aniline in a 64% yield. The picrate was purified from aqueous ethanol.

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S,S-Disubstituted Sulfonium Dicyanomethylides

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Synthesis and structure of stable sulfonium ylides containing the dicyanomethylide moiety is discussed. Three methods of preparation are presented along with the limitations of each. Physical properties of twelve sulfonium dicyanomethylides are listed. A brief study of the chemical properties of sulfonium dicyanomethylides has shown these compounds to be inert compared with previously known classes of sulfonium ylides. Specifically, they do not react with olefins or carbonyl reagents under conditions of the Wittig Reaction.

The class of compounds known as ylides encompasses zwitterions of the type ($^+YCR_2{}^-$) where Y is either R_3P–, R_3N–, R_3As–, or R_2S–. Generally speaking, these compounds are unstable and are usually proposed as intermediates in various rearrangement and elimination reactions.[2–6] In the course of work on cyano compounds, we became interested in sulfonium ylides which were substituted with cyano groups. Of the sulfonium ylides previously described in the literature, only those which bore an aromatic group on the α-carbon could be isolated, and even these were relatively unstable. These included the fluorenyl-,[7] substituted fluorenyl-,[8] and phenylsulfonium[9] ylides. Nonaromatic sulfonium ylides of the type prepared by Corey[4] were stable only in solution and at low temperatures. We wish to report now the synthesis of a new class of ylides, the sulfonium dicyanomethylides, which are unique in their chemical and thermal stability.

This new class of sulfonium ylide can be represented by the following structures. The simplest member of the class, the dimethyl derivative was first prepared by the condensation of dimethyl sulfoxide with malononitrile in the presence of hydrogen chloride or thionyl chloride. The resulting dihydrochloride was then neutralized with base to give the free ylide in 41% yield

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