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On Acylhalogenamine Derivatives and the Beckmann Rearrangement

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On Acylhalogenamine Derivatives and the Beckmann Rearrangement.

BY EDWIN E. SLOSSON.

A. W. Hofmann's[1] well-known method for preparing amines by converting acid amides into acid bromamides and treating the latter with aqueous alkali, involves a molecular rearrangement of the acid bromamides which, as Hoogewerff and van Dorp[2] later pointed out, is a perfect parallel of the Beckmann rearrangement of the oximes. In both cases an alkyl or alphyl radical (R) leaves the carbon atom holding the nitrogen halide (NHX), or the oxime (NOH) group, and attaches itself to the nitrogen atom, while the negative atom (Cl, Br), or group (OH), originally held by the nitrogen, oxidizes the carbon atom in question. The following equations give summarily the course of the reactions:

$$\mathrm{RCO.NHBr} \rightarrow \mathrm{BrCO.NHR} \rightarrow \mathrm{CO:NR} + \mathrm{HBr};$$
$$\mathrm{R'RC:NOH} \rightarrow \mathrm{R'C(OH):NR} \rightarrow \mathrm{R'CO.NHR}.$$

The mechanism of these interesting molecular rearrangements has been the subject of some investigation and quite a little speculation.[3] In a study of the nature and cause of the rearrangement, attention was called by Prof. Stieglitz to the desirability of determining experimentally to what extent, if at all, the hydrogen atom in the acid bromamide group, —CONHBr, is necessary for effecting the rearrangement of the acid bromamides. According to his views "an alkali

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[1] Ber. d. chem. Ges., **14**, 2725 (1881); **15**, 408 (1882).

[2] Rec. trav. chim. Pays-Bas, **6**, 376 (1887).

[3] Hofmann: *Loc. cit.*; Hoogewerff and van Dorp: Rec. trav. chim. Pays-Bas, **15**, 107 (1896). Freundler: Bull. Soc. Chim., **17**, 421 (1897); Nef: Am. Chem. J., **18**, 753 (1896), Note. Ann. Chem. (Liebig), **298**, 308 (1897); **318**, 39, 227 (1901). See in particular, Stieglitz: On the "Beckmann Rearrangement," Am. Chem. J., **18**, 751 (1896); **29**, 49 (1903).

might cause an acid bromamide, RCONHBr, to lose hydrobromic acid directly, thus producing a body, (RCO)N<, with a univalent nitrogen atom, the reactivity of which must then be the cause of the peculiar separation of the alkyl radical, R, from the carbon atom holding the nitrogen ; the very reactive univalent nitrogen atom taking the alkyl radical away from the carbon atom, isocyanates must result, and these have actually been obtained as the first tangible products of the reaction." The formation of an isocyanate as the first product of the rearrangement is also in accord with the production of the most important compounds finally obtained from acid bromamides under varying conditions, *viz.*, amines by the action of hot dilute alkalies,[1] carbamates, RNHCOOK, in the presence of cold concentrated alkali,[2] and urethanes[3] in the presence of alcohols.

At the suggestion and under the direction of Professor Stieglitz, I undertook[4] the investigation of the problem whether the Beckmann rearrangement could still proceed or would be prevented when the hydrogen atom necessary for the breaking off of hydrobromic acid had been replaced by an alkyl or an alphyl group.

The investigation had to concern itself with the two possible classes of such derivatives. In the first place we could have acylhalogenalkyl(alphyl)amines in which both the alkyl (alphyl) and the halogen are attached to the nitrogen atom, as in RCO.(NHalR′). In the second place we could have the halogen imido ethers RC(: NHal)OR′, isomeric with the first series, the alkyl (alphyl) group, R′, being attached to the oxygen atom. The work done on the former class of compounds will be discussed first.

When this investigation was begun only two or three compounds of this class were known. These were notably acetyl-

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[1] Hofmann : Ber. d. chem. Ges., **15**, 411, 412 (1882).

[2] Hoogewerff and van Dorp : *Ibid.*, **20**, Ref. 470 (1887).

[3] Stieglitz and Lengfeld: Am. Chem. J., **15**, 215, 504 (1893).

[4] This work was begun in 1895 and has been continued, chiefly in summer vacations, ever since. A preliminary paper was published in 1896 (Ber. d. chem. Ges., **28**, 3266) to hold the field, and notices of the progress of the investigation have appeared at intervals (Am. Chem. J., **18**, 753 (1896) ; Ber. d. chem. Ges., **34**, 1613 (1901) ; Proc. Chem. Soc. (London), **16**, 1 (1900), etc.)

ethylchloramine prepared by Tscherniak and Norton,[1] and acetylchloranilide obtained by Bender.[2] Analogous bromine derivatives were not known. The methods used by the chemists mentioned failed to give good results in the preparation of other derivatives of this class, and of bromine compounds,[3] in particular, as most of these compounds are extremely sensitive to change by the action of acids, by reduction, by hydrolysis, or in the case of derivatives of the aromatic amines, by rearrangement into the acyl derivatives of halogen anilines, $H_2N(C_6H_4Hal)$. A careful study was first undertaken, therefore, to develop the special conditions and precautions for isolating these acyl halogen amides. As will be shown in the experimental part, this study was successful, both experimentally and in supplying the theoretical basis for correct work.

In the next place it was found necessary to make an experimental determination of the constitution of these acylhalogenalkyl(alphyl)amines, to decide between the two possible constitutions :

$$\underset{\text{I.}}{RCO.(NHalR')} \qquad \text{and} \qquad \underset{\text{II.}}{RC(OHal)(:NR')}$$

Although important theoretical conclusions were based[4] on the generally accepted constitution (I.), it really had never been proved rigidly, and it was open, if not to decided objection, at least to serious doubt. Its general acceptance seems to have been based chiefly on the idea that in an acyl anilide, such as acetanilide, $CH_3CONHC_6H_5$, the nitrogen atom still holds a hydrogen atom, as in aniline, and that such a compound must, by substitution, under the influence of hypochlorous acid, give a nitrogen halide, $CH_3CO.NClC_6H_5$. It has, however, been proved that acyl amides and anilides frequently do give oxygen derivatives.[5] For instance, Comstock

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[1] Bull. Soc. Chim., **30**, 106 (1878).

[2] Ber. d. chem. Ges., **19**, 2272 (1886).

[3] See, for example, Castoro: Gazz. chim. ital., **28**, 312 (1898); Oechsner de Coninck : Compt. rend., **126**, 907, 1042 (1898).

[4] See, for example, Norton and Tscherniak : *Loc. cit.*, p. 106; Armstrong : J. Chem. Soc. (London), **77**, 1051 (1900); Chattaway and Orton: *Ibid.*, **75**, 1046 (1899); etc.

[5] Comstock, Kleeberg, Wheeler, and others : Am. Chem. J., **12**, 493 (1890); **13**, 520 (1891); **19**, 129 (1899); etc. Tafel and Enoch : Ber. d. chem. Ges., **23**, 105 (1890) Stieglitz and Dains : J. Am. Chem. Soc., **21**, 135 (1899).

and Kleeberg showed that formanilide forms a silver salt from which methylphenylimidoformate, $HC(OCH_3)NC_6H_5$, is obtained by the action of methyl iodide. The metal salts undoubtedly have an analogous constitution.[1] On finding that silver formanilide gave with iodine, under the same circumstances as in the previous reaction, formyliodaniline, Comstock suggested that the iodine derivative could very well have a constitution analogous to that of the imido ethers, *viz.*, $HC—(OI) : NC_6H_5$, and since the iodide has the same properties as all the acylchlor- and bromanilides, it is obvious that the constitution of the latter bodies could not be based on their formation from acyl anilides. Their properties of being chlorinating or brominating agents, of being susceptible to hydrolysis, and of being readily rearranged into acyl derivatives of chlorinated or brominated anilines, $NH_2(C_6H_4X)$, would agree equally well with either of the above constitutions (I. and II.). If the bodies were not really nitrogen halides, $RCON(Hal)R'$, however, any deductions in regard to the "Beckmann rearrangement," as based on their behavior, would obviously have been impossible, and so a rigid experimental proof was sought at once, which would decide between constitutions I. and II.

In our first attempts to settle the question of the constitution of these bodies their behavior was such as to throw considerable doubt on their being nitrogen halides. We found first that the acyl halogen anilides do not form any cyanogen derivatives with potassium cyanide according to the equation :

$$CH_3.CO.N(Hal).C_6H_5 + KCN \rightarrow CH_3.CO.N(CN).C_6H_5 + KHal,$$

but are always reduced to the acyl anilides. On the other hand, undoubted nitrogen chloride derivatives, like the chlordialkylamines, R_2NCl, easily give cyanamides under exactly the same conditions.[2]

$$R_2NCl + KCN \rightarrow R_2N.CN + KCl.$$

In order to make sure that the right conditions were present for Berg's reaction, the method was tried on chlorpiperidine, and cyanpiperidine was obtained without difficulty.

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[1] Hantzsch : Ber. d. chem. Ges., **34**, 3142 (1901) ; **35**, 228 (1902).

[2] Berg : Ber. d. chem Ges , **26**, 188 (1893), Ref.

Secondly, it appeared from many experiments that the acylhalogenalkyl(alphyl)amines, by treatment with zinc ethyl, are simply reduced and not alkylated; for instance, the reaction

$$2R—CO—N(Hal)—C_6H_5 + Zn(C_2H_5)_2 \rightarrow 2RCO—N(C_2H_5)(C_6H_5) + ZnHal_2$$

does not take place. But an undoubted nitrogen chloride derivative, ethyldichloramine, $C_2H_5—NCl_2$, is known to give, with zinc ethyl, triethylamine.[1]

The last way taken for establishing the constitution of the acylhalogenalkylamines led to the following simple solution of the question.[2] If acetylamylamine is treated with hypochlorous acid, the corresponding acetylchloramylamine is formed:

$$CH_3CO—NH—C_5H_{11} + HOCl \rightarrow CH_3CO—NCl—C_5H_{11} + H_2O.$$

The same compound is obtained when amylchloramine[3] is acetylated by means of acetic anhydride,

$$C_5H_{11}—NHCl + (CH_3CO)_2O \rightarrow CH_3CO—NCl—C_5H_{11} + C_2H_4O_2.$$

This result proves that the acylhalogenalkylamines and anilides are really nitrogen halides, that is, derivatives of Hofmann's acid chlor- and bromamides, RCO(NHHal), and that the constitution, RC(OHal)(NR′), suggested by Comstock as a possible one for them, may now be excluded without hesitation as far as the chlorine and bromine compounds are concerned.[4]

Two parts of the work on the first class of alkyl (alphyl) derivatives of the acid halogen amides, *viz.*, the determination of the special conditions for preparing them and the determination of their constitution, having been disposed of, it only

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[1] Tscherniak: *Ibid.*, **9**, 148 (1895).

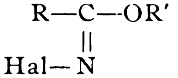
[2] Stieglitz and Slosson: *Ibid.*, **34**, 1615 (1901).

[3] Berg: Bull soc. chim., [3], **3**, 687 (1890).

[4] So little is known about the corresponding iodine derivatives, and the character of hypoiodous acid approaches so near that of a base that no conclusion as to the constitution of Comstock's formiodanilide should be based on the above work with hypochlorous acid. Formiodanilide may very well stand closer to silver formanilide than to formchloranilide. J. STIEGLITZ.

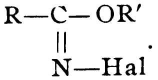
remained to test whether such compounds could be made to suffer the "Beckmann rearrangement" which the mother-substances, the acid halogen amides, RCO—NH—Hal, undergo so readily. A large number of experiments with all varieties of acylhalogenalkylamines and acylhalogenalphylamines led to the important conclusion that in no case could a Beckmann rearrangement be effected. In some cases, for example, with benzchloranilide, $C_6H_5.NCl.C_6H_5.CO$, it was possible to show that the rearrangement did not occur even to a minimal extent, since not even traces of diphenylamine, which is easily detected, could be found.

It was shown above, (page 4) that the acid halogen amides must give by replacement of the hydrogen atom of the group —CONHHal, besides the alkylated (alphylated) nitrogen derivatives —CO(NRHal) just discussed, a second class of isomeric ethers, —C(OR)(: NHal), whose relation to the Beckmann rearrangement was included in this investigation. In contrast to the bodies just dealt with, these imido ethers presented a comparatively simple problem. The methods for their preparation and their constitution had been definitely established by Stieglitz,[1] who prepared methyl chlor- and bromimidobenzoate, and they had been proved by him to be most remarkable for their stability as nitrogen halides. My work on these bodies was chiefly directed towards the preparation of stereoisomers and the effecting of the Beckmann rearrangement. On the basis of Hantzsch and Werner's[2] theory of stereoisomerism (syn and anti) produced by a doubly-linked nitrogen atom, as in the oximes, the halogen imido ethers might exist in the two stereoisomeric forms,



$$\begin{array}{r}\mathrm{R—C—OR'}\\ \| \quad\quad\\ \mathrm{Hal—N}\quad\quad\end{array}$$

and



$$\begin{array}{l}\mathrm{R—C—OR'}\\ \quad\ \|\\ \quad\ \mathrm{N—Hal}\end{array}.$$

Only the former class would be expected to be directly capable of undergoing a Beckmann rearrangement of the molecule.[3] Although solid chlorimido ethers of admirable stability were obtained, all efforts at recognizing stereoisomers,

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[1] Am. Chem. J., **18**, 751 (1896).

[2] Ber. d. chem Ges., **25**, 33 (1892); **29**, 1146 (1896).

[3] Werner: *Loc. cit.*

or at converting the compounds obtained into other modifications, resulted in failure.[1] None of the halogenimido ethers investigated gave the least sign of undergoing the Beckmann rearrangement.

It would appear, therefore, that the presence of the hydrogen atom (H') of the acylamine halides, RCO—NH'Hal, is essential for the successful "Beckmann rearrangement" of the molecules, since neither class of their alkyl derivatives is capable of undergoing the rearrangement in question.

EXPERIMENTAL PART.

The Preparation of Alphylacylhalogenamines.

The successful preparation of the chlorine and bromine compounds of this class was found to be dependent on observing a number of interesting conditions, which follow from the peculiar tendency of these bodies to suffer chemical change. Bender had obtained phenylacetylchloramine by treating acetanilide with an aqueous extract of bleaching-powder and acidulating the mixture with acetic acid. His directions are so indefinite that some chemists have failed entirely to prepare phenylacetylchloramine by his process. For example, Castoro[2] says Bender's reaction is impossible and that he gets by all possible variations of the proportions of acetanilide, acetic acid, and hypochlorite no active nitrogen halide derivatives but only two inactive bodies, parachloracetanilide and a dichloracetanilide.[3] While, as a matter of fact, the active acetylchloranilide can readily be obtained by following Bender's directions carefully, neither the yield nor the purity of the compound is satisfactory. The method failed utterly in attempts to use it for preparing analogous active nitrogen bromide compounds of the acylanilides,[4] only inac-

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[1] Like failure, it will be remembered, has so far attended all efforts of Hantzsch and others to prepare stereoisomeric derivatives, : C : NX, in which X was, for instance, C_6H_5—, —COOR, or any group in fact other than —OH (the oximes) or —NHAlphyl (the hydrazines). Ber. d. chem. Ges., **27**, 1248 (1899), etc.

[2] Gazz. chim. ital., **28**, 312 (1898) ; compare Armstrong : J. Chem. Soc. (London), **77**, 1047 (1900).

[3] Oechsner de Coninck (Compt. rend., **126**, 907, 1042 (1898)) obtained no nitrogen halides by the action of hypochlorites on amides and amines.

[4] Slosson : Ber. d. chem. Ges., **28**, 3266 (1896) ; see also Seliwanow : *Ibid.*, **25**, 3620 (1892) ; Jacoby : J. prakt. Chem., [2], **37**, 50 (1888).

tive derivatives of the bromanilines resulting with the bromine attached to the benzene nucleus of the anilines.

The first fact of which cognizance must be taken in the preparation of these nitrogen halides is that the reaction by which they are formed is reversible :[1]

$$\mathrm{RCO{-}NHR'} + \mathrm{HOHal} \rightleftarrows \mathrm{RCO{-}NHalR'} + \mathrm{H_2O}.$$

The mass law requires, therefore, an excess of hypochlorous or hypobromous acid to effect a tolerably complete transformation except in those cases where the product is very insoluble. In going from the derivatives of hypochlorous to hypobromous and hypoiodous acid, the hydrolysis of the above nitrogen halides by water seems to become progressively more marked, and, therefore, to play a more important rôle in their preparation, as the atomic weight of the halogen increases. This was verified experimentally. The phenylacylbromamines were found by me to stand between the analogous chlorine and iodine derivatives. Phenylacetylchloramine is rather stable even towards boiling water, phenylacetylbromamine can be prepared in the presence of water, but it is slowly decomposed, even at ordinary temperatures, by water (see below), and phenylformyliodamine could be prepared[2] only when water was carefully excluded.

In the next place, where R′ in the above reaction is an aromatic radical, the nitrogen halide with its reactive halogen atom is very readily transformed into the stable isomeric acyl derivative of the halogenated anilines, according to

$$\mathrm{RCO.NHalC_6H_5} \rightarrow \mathrm{RCO.NH(C_6H_4Hal)}.$$

As the latter reaction is non-reversible, the preparation of the nitrogen halides may prove an utter failure if this transformation is not prevented. This is the chief source of failure in making these compounds. The transformation was found to proceed gradually under the influence of moisture, and very

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[1] Selıwanow : *Loc. cit.*

[2] Comstock and Kleeberg : Am. Chem. J., 12, 500 (1890).

much more rapidly by the action of acids. It is also caused by the action of heat.[1]

As the phenylacylbromamines are much more sensitive to water and acids (see below) than the chloramines, only their transformation-products are obtained if acids even of ordinary weakness (*e. g.*, acetic acid) are used in preparing them. The hypobromous acid necessary for their formation must be liberated by such weak acids as boric acid[2] or carbonic acid,[3] the concentration of whose hydrogen ions can be still further diminished by using a bicarbonate, or carbonic acid in the presence of a bicarbonate.

In the last place it follows from the above discussion that in the purification of these nitrogen halides by recrystallization, aqueous solvents and moisture must be rigidly excluded, besides, obviously, such solvents as are very easily chlorinated or brominated.

The conditions, then, for successfully preparing even rather unstable representatives of the alphylacylhalogenamines are

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[1] The first two influences are undoubtedly identical fundamentally, water being an exceedingly weak acid. The slow transformation under the influence of water, the vastly increased rate of change in the presence of acids, and the fact that a number of these compounds when dry (see pages 304–5 below) are comparatively stable towards heat and are only very slowly transformed by it, indicate that in aqueous solution this transformation is due rather to a sequence of two reactions, *viz.*:

$$\mathrm{RCO.NHalC_6H_5 + H_2O \rightleftarrows RCO.NHC_6H_5 + HOHal} \quad (1),$$

and

$$\mathrm{RCO.NHC_6H_5 + HOHal \rightarrow RCO.NHC_6H_4Hal + H_2O} \quad (2),$$

than to a direct molecular rearrangement or migration of atoms:

$$\mathrm{RCO.NHalC_6H_5 \rightarrow RCO.NHC_6H_4Hal} \quad (3).$$

As the acylalphylbromamides are much more sensitive to water and acids than the chlorides, we find in this behavior the reason why they were never successfully isolated and the transformation-products alone were obtained, until in 1896 Slosson and I avoided the use of any but the weakest acids in preparing them. (See Stieglitz and Slosson: Ber. d. chem. Ges., **28**, 3267 (1896); Proc. Chem. Soc. (London) **16**, 1 (1900); Armstrong: J. Chem. Soc. (London). **77**, 1047 (1900); Chattaway and Orton: *Ibid.*, **77**, 134 (1900)). Whether the transformation under the influence of heat is due to a molecular rearrangement or, rather, to a mutual chlorination (bromination) of two molecules,

$$\mathrm{2RCO.NHalC_6H_5 \rightarrow 2RCO.NHC_6H_4Hal},$$

remains an open question, which could be decided by determining the velocity of the reaction. Since this was written Blanks has shown by velocity determinations that the reaction consists of a monomolecular rearrangement. Rec. trav. chim. Pays-Bas., **21**, 366 (1902). See also Armstrong: *Loc. cit.* J. Stieglitz.

[2] Slosson: *Loc. cit.*

[3] Slosson: *Loc. cit.*; Chattaway and Orton: J. Chem. Soc. (London), **75**, 1046 (1899), etc.; Küster: Ztschr. Elektrochem., **4**, 110.

the use of a considerable excess of the hypo acid, the exclusion of more than minimal quantities of hydrogen ions, best obtained from very weak acids, and the exclusion of moisture in the process of purification. The avoidance of an unnecessary rise of temperature may be added as a further precaution.

For chlorinating compounds insoluble in water the following method was found useful : Thirty grams of sodium hydroxide are dissolved in 100 cc. of water and a weighed amount of chlorine, nearly enough to saturate it, is absorbed in the cold solution. With ordinary caustic soda, which has been exposed to the air and therefore has taken up some water and carbonic acid, between 20 and 24 grams of chlorine may safely be absorbed, but the operation must be stopped before decomposition sets in through an excess of chlorine. A solution so prepared contains very nearly the theoretical amount of active chlorine, one-half the total. It can be kept in a cool place for several days without material loss of strength. If to a sufficient quantity of this solution be added the calculated amount of the amide dissolved in alcohol, which is saturated with boric acid, the chlorine compound is precipitated on diluting with water, and can be filtered by suction and dried on a porous clay plate ; or, if it is very unstable, the reagents may be mixed in a separatory funnel, together with powdered ice, and the nitrogen halide extracted at once with ether. Bromine compounds can be made in the same way, by using a solution prepared by dissolving bromine in a slight excess of potassium hydroxide solution, or by shaking it with mercuric oxide and water.

All the nitrogen halides set free iodine, either from potassium iodide or from hydriodic acid, and they can be analyzed by dropping them into a slightly acidified solution of potassium iodide and titrating the released iodine with a N/10 solution of thiosulphate. Where the compound is very insoluble in water, it is necessary to dissolve it in alcohol or in a mixture of ether and alcohol. The determination of the halogen as silver halide does not necessarily indicate the purity of the compound in the case of anilides and naphthalides, because the isomers with halogen in the ring, which are the chief impurities, give by Carius' method the same analytical figures as the nitrogen halides. It is best to titrate the iodine as quickly as possible, for there are sometimes secondary reactions with the free iodine which cause too low results.[1]

Phenylacetylchloramine (*Acetylchloraminobenzene*),
$CH_3CO—NClC_6H_5$.

This compound may be formed in acid, alkaline, or neutral solutions of hypochlorites, but a slightly alkaline solution is best, and, after trying a great many methods, the following was found to give the most satisfactory results:[2] Twenty grams of acetanilide are dissolved in 4 liters of water and the solution cooled to at least 10°. Chlorine is passed into a cold solution of sodium carbonate (10 per cent) until a test with a few cubic centimeters shows that the solution will precipitate ten times its volume of the acetanilide solution; then the required quantity of this hypochlorite solution is poured into the acetanilide solution and shaken. The chlorine compound comes down at once as a flocculent precipitate. It is filtered, washed, and dried. The yield is 20 to 24 grams (theoretical 25 grams). If the hypochlorite solution is deficient in strength or quantity, the precipitate forms slowly in fine needles, isolated or in bundles. If too strongly alkaline, the solution turns brown, has the odor of isocyanide, and the chlorine compound reverts to acetanilide. If the solution is too strongly acid, or if there is much free chlorine, parachloracetanilide is the sole product. Phenylacetylchloramine is quite stable when pure and dry, and it can be preserved for days without material decomposition. It melts at 91°.

0.2463 gram substance required 28.98 cc. N/10 thiosulphate.

	Calculated for C_8H_8NOCl.	Found.
Cl	20.91	20.86

A great many experiments were made on the decomposition of phenylacetylchloramine with potassium hydroxide and sodium methylate, but in no case was it possible to detect

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[1] Compare Behrend and Schreiber: Ann. Chem. (Liebig), **318**, 381 (1901).

[2] For other methods, see Bender: Ber. d. chem. Ges., **19**, 2272 (1886); Chattaway and Orton: J. Chem. Soc (London), **79**, 277 (1901); Armstrong: *Ibid.*, **77**, 1047 (1900).

methylaniline or any derivative of it, which would be the product if a Beckmann rearrangement had taken place. From 18 to 30 grams of the substance were used in each test, but acetanilide was the sole product identifiable whether the reaction-product was worked out by precipitation, extraction, or distillation. Both hot and cold solutions of potassium hydroxide were used, and both 10 and 20 per cent strengths. When hot strong alkali was used, the solution turned brown and had a disagreeable odor, apparently of isocyanide, and there was a little tarry matter formed. The acetanilide was, however, recovered almost quantitatively in every case in a nearly pure state, and from the slight residues the only basic compound obtained after saponification was aniline in which no methylaniline could be detected.

A series of experiments with solutions of sodium methylate, cold and hot, strong and weak, gave similar results, and none of the products of a Beckmann rearrangement could be found. Even when 30 grams of the chlorine compound were used, acetanilide was the sole product in quantity sufficient to identify, although there was evidence of further decomposition in the red color of the extract in ligroin, which in acid alcohol gave a purple solution of great tinctorial power.

Methyl Phenylmethylcarbamate, $(C_6H_5NCH_3)COOCH_3$.—As this compound is one which might result from a Beckmann rearrangement of phenylacetylchloramine with sodium methylate, its properties were determined by preparing it. Redistilled methylaniline (16 grams) was shaken with the same volume of water to an emulsion, and to the solution cooled to 0° was added 7 grams of methyl chlorcarbonate from small bulbs with capillary tubes. The mixture was warmed for half an hour, then cooled, and hydrochloric acid added to acid reaction. The ether extract was dried over calcium chloride and distilled twice. The product, the methyl ester of phenylmethylcarbamic acid, is a light-yellow oil, easily soluble in ether and ligroin. It is dissolved by heating it in concentrated hydrochloric acid but is not attacked by a solution of sodium hydroxide. It has a fishy odor and boils at 235°.

0.4070 gram substance gave 44 cc. N at 25° C. and 743.8 mm.

	Calculated for $C_9H_{11}O_2N$.	Found.
N	8.42	8.43

Several attempts were made to replace the chlorine atom in phenylacetylchloramine with an ethyl radical by the use of zinc ethyl,[1] but in no case was there evidence of such a reaction.

Dry phenylacetylchloramine (14 grams) was dropped gradually into a solution of zinc ethyl (5 grams) in absolute ether in a flask fitted with a reflux condenser. At each addition of the chloranilide there was an evolution of a gaseous hydrocarbon, which was collected but not analyzed. A stream of carbon dioxide was carried through the apparatus during the operation. At the end the ether was evaporated and water added. Repeated extraction of the acid and alkaline solution with ether gave acetanilide as the only product, and this, when purified, amounted to 11.3 grams. Repeating the experiment with the same quantities of the reagents, parachloracetanilide was the chief product obtained. Evidently the molecular transformation was caused by the energy liberated in the reaction. In the residues the products of saponification, acetic acid and aniline were found in small quantity, but no derivatives of ethylaniline which would result from the substitution of chlorine by that radical or methylaniline from a Beckmann rearrangement could be detected.

Phenylacetylchloramine (13 grams) dissolved in 50 per cent alcohol and treated with potassium cyanide (5 grams) gave acetanilide and parachloracetanilide as the sole products. There was no evidence of the substitution of chlorine by cyanogen according to Berg's reaction.[2]

Piperidyl Cyanide by Berg's Reaction.—In order to test the generality of Berg's reaction and to assure myself that I understood the conditions under which it took place, piperidyl cyanide was prepared by the following method.[3] Six grams of chlorpiperidine, prepared by dropping 10 grams of piperi-

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[1] Tscherniak : Bull. soc. chim., [2], **25**, 166 (1896) ; Ber. d. chem. Ges., **9**,148 (1896).

[2] Ann. chim. phys., [7], **3**, 353 (1894).

[3] The same cyanide has since been prepared in another way by Wallach and Samann : Ber. d. chem. Ges., **32**, 1873 (1899).

dine into a boiling solution of bleaching-powder,[1] was dissolved in alcohol and treated with 3 grams of potassium cyanide in fine powder. The reaction takes place immediately and the alcohol is heated to boiling. After distilling off the alcohol, taking up the residue with ether, and drying it over potassium hydroxide, the piperidyl cyanide was distilled in a vacuum (30 mm.) between 122° and 124° C. It is a colorless, fragrant oil, insoluble in water.

The identity of the piperidyl cyanide was proved by converting it into piperidyl urea by heating it with 50 per cent sulphuric acid for half an hour on a water-bath. After neutralizing the solution with sodium hydroxide and extracting the mixture with ether, the urea was obtained by evaporation of the ether. It was recrystallized from water and compared with piperidyl urea made by Cahours' method.[2] A mixture of the two preparations melted at the same point (103° C.).

Parachloraniline.—On account of the ease with which the chlorine in acetylchloranilide can be made to enter the para position and the resulting compound can be saponified, use can be made of this reaction in the preparation of *p*-chloraniline. For making this in quantity, the following process was found more convenient than the methods published: Dissolve 10 to 15 grams of acetanilide in a liter of water, cool somewhat, and pass in chlorine as long as the white precipitate of *p*-chloracetanilide is formed. Filter and heat the chloracetanilide for an hour at 150°, with enough concentrated sulphuric acid to dissolve it. Pour the mixture into water, make the solution alkaline with some hydroxide to precipitate most of the parachloraniline, and extract the filtrate with ether to get the rest. Purify the compound by dissolving it in water, boiling the solution with animal charcoal, and filtering. By concentrating the water solution, parachloraniline crystallizes out in cubes or needles. The yield is almost quantitative.

Phenylacetylbromamine (*Acetylbromaminobenzene*), $CH_3CO(C_6H_5NBr)$.—This compound was first made by adding a solution of potassium hypobromite to a saturated aqueous solu-

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[1] Lellmann and Geller: *Ibid.*, **21**, 1922 (1888).

[2] Ann. chim. phys., [3], **38**, 84 (1853).

tion of acetanilide and then passing a stream of carbon dioxide into the solution. If the acetanilide solution contains borax or boric acid, the bromine compound is precipitated without using carbon dioxide. A saturated solution of acetanilide, prepared by dissolving about 5 grams in a liter of water and saturating it with borax and boric acid, is cooled to 0° and filtered. To this is added an excess, even twice the theoretical amount, of hypobromite solution made by dissolving bromine in 10 per cent potassium hydroxide. If both solutions are kept cold, best with powdered ice, the phenylacetylbromamine is slowly precipitated, and after filtering can be freed from a small quantity of parabromacetanilide by fractional crystallization from ether or ligroin. It is precipitated in yellow flakes or four-pointed stars, and melts at 94° to 95°, changing to parabromacetanilide.

0.1748 gram substance required 16.32 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	37.34

This bromacetanilide is very much more unstable than the corresponding chlorine compound, and changes into parabromacetanilide in a few minutes when in warm and moist air. With ammonium hydroxide it gives off nitrogen as do all the compounds of this class. In numerous experiments with this compound only the two forms of decomposition were observed: with acids, it is transformed to parabromacetanilide, and with alkalies acetanilide is regenerated. None of the products of a Beckmann rearrangement were ever found.

Phenylformylchloramine (*Formylchloraminobenzene*), $HCO.NClC_6H_5$.—This compound is precipitated in crystalline form by adding a solution of hypochlorous acid, made by running chlorine into a 10 per cent solution of sodium carbonate, to an ice-cold, saturated, aqueous solution of formanilide and shaking violently. The strength of the hypochlorous solution is ascertained by titration and an excess is used. The substance melts at 44°. It can be heated even to 120° without much decomposition. Above this temperature it gives off acid vapors accompanied with a slight odor, apparently of isocyanate. It can be recrystallized from ether, ligroin, or acetic acid, but it decomposes violently with ammonia, or when heated with absolute alcohol. Hydrochloric acid and many other reagents convert it into the isomeric formyl-*p*-chloranilide.

0.1273 gram substance required 16 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONCl.	Found.
Cl	22.79	22.34

For comparison, formyl-*p*-chloranilide was also made by boiling 1 gram parachloraniline with 3 grams formic acid for half an hour. The excess of formic acid is distilled off and the residue poured into cold water. . It melts at 101° C. It is soluble in ether, chloroform, or hot water, but insoluble in ligroin. Recrystallized from ether it forms colorless parallelograms with diamond markings, similar in form to methylbenzamide.

Phenylformylbromamine (*Formylbromaminobenzene*), $HCO—NBrC_6H_5$.—To prepare this a one per cent solution of formanilide in water, saturated with boric acid, is cooled to 0° and a little more than the calculated quantity of potassium hypobromite solution is added. Instead of using boric acid, a stream of carbon dioxide may be run in after the addition of the hypobromite. In either case a light-brown precipitate of formylbromaminobenzene is slowly formed, which can be recrystallized from ether or ligroin in needles which are only slightly yellow and melt at 79° to 80°. The compound decomposes spontaneously even in dry air, and attacks ammonia water violently, giving off nitrogen. By acids, alkalies, and heat it is readily converted into parabromformanilide (m. p. 119°).

0.1678 gram substance required 16.6 cc. N/10 thiosulphate.

	Calculated for C_7H_6ONBr.	Found.
Br	39.95	39.55

Phenylbenzoylchloramine (*Benzoylchloraminobenzene*), $(C_6H_5CO)NClC_6H_5$.—The insolubility of benzanilide in water makes it rather difficult to prepare the chlorine derivative by the customary methods,[1] but the following procedure gives a good yield of excellent purity. Two grams of benzanilide are dissolved in 200 cc. of alcohol with 10 grams of boric acid. To this is added 10 cc. of a solution of sodium hypochlorite containing 0.07 gram or more of active chlorine per cubic centimeter, both solutions being kept cold. After shaking and filtering the mixture with the pump, water is added and the benzoylchloraminobenzene appears as a white, flocculent precipitate. It is filtered and dissolved in ether. On adding light ligroin and evaporating the mixture in a vacuum-desiccator it forms large, transparent crystals.

0.1091 gram substance required 9.39 cc. N/10 thiosulphate.

	Calculated for $C_{18}H_{10}NOCl$.	Found.
Cl	15.30	15.22

The substance is easily soluble in ether and alcohol but less soluble in ligroin. It melts, without decomposition, at 81°.5 to 82°,[1] and it is still active with potassium iodide after it has been heated to 160° and turned slightly yellow. Above this temperature it becomes rapidly darker and gives off a little vapor, which is, judging from its odor, benzoyl chloride. The chief substance formed, however, is parachlorbenzanilide. This compound is also the result of boiling with water. Ammonium hydroxide attacks the nitrogen halide slowly in alcoholic solution.

Phenylbenzoylchloramine dissolved in alcohol and treated with a little sodium hydroxide and warmed, is reduced at once to benzanilide, as was proved by taking the melting-point of the reaction-product mixed with known benzanilide. The crude product of the reaction tested for diphenylamine by hydrochloric and nitric acids gave no coloration. A portion of the same mixture, to which a minute particle of diphenylamine had been added, gave an intense indigo-blue. So it is positive that the Beckmann rearrangement does not take place to the slightest extent.

For comparison with the product obtained from benzoylchloraminobenzene by the migration of the chlorine atom from

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[1] Slosson : Ber. d. chem. Ges., 28, 3269 (1896) ; Chattaway and Orton : J. Chem. Soc. (London), 75, 1053 (1899). They give the melting-point as 77°.

the nitrogen to the aromatic nucleus, parachlorbenzanilide was prepared from benzoyl chloride and parachloraniline. When recrystallized from hot water, it appeared in fine cubical crystals. It had the melting-point 187° to 187°.5, instead of 183° to 184° as reported by Hantzsch.[1]

Paratolylformylchloramine (*Formylchloramino-p-toluene*), $CHO.NClC_6H_4CH_3$.—Adding 20 cc. of a 10 per cent solution of formyl toluide in alcohol with a little acetic acid to 100 cc. of a solution of bleaching-powder (1 cc. = 0.008 gram chlorine) precipitates formylchlortoluide. When dissolved in hot ligroin, it separates, on cooling, in beautiful clusters of crystals, melting at 49° to 50° and decomposing at 140°.

0.1122 gram substance required 13.09 gram N/10 thiosulphate.

	Calculated for C_8H_8NOCl.	Found.
Cl	20.94	20.77

Paratolylformylbromamine (*Formylbromamino-p-toluene*), $CHO—NBrC_6H_4CH_3$(*p*).—To prepare this a saturated solution of formyl paratoluide in water is added to an ice-cold solution of potassium hypobromite until a flocculent precipitate is formed. The bromine compound slowly forms in flakes by shaking. It is filtered rapidly, dissolved in a very little ether, several times its volume of light ligroin is added, and the solution is quickly evaporated by a blast or by a vacuum-pump. It is pure white and melts at 80°, decomposing at slightly higher temperatures. It is extremely unstable and rapidly turns red on exposure to moist air, giving off free bromine.

0.1314 gram substance required 11.60 cc. N/10 thiosulphate.

	Calculated for C_8H_8ONBr.	Found.
Br	37.35	35.30

α-Naphthylformylchloramine (*Formylchloramino-α-naphthalene*), $HCO—(C_{10}H_7NCl)$.—Adding an alcoholic solution of formyl-α-naphthalide with a little acetic acid to a large amount of calcium hypochlorite solution gives, after a few minutes' shaking in the cold, a precipitate of the chloramine. It is

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[1] Ber. d. chem. Ges., **24**, 56 (1891).

very soluble in chloroform but crystallizes best from ligroin. The melting-point is 63°. It is extremely unstable, as it is decomposed quickly by water at ordinary temperatures. An ethereal solution, brought over caustic potash to dry it, is at once attacked, the ether boiling and turning red.

0.1146 gram substance required 9.8 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	15.13

β-Naphthylformylchloramine (*Formylchloramino-β-naphthalene*), $HCO—(NClC_{10}H_7)$.—Adding an alcoholic solution of formyl-*β*-naphthalide, acidified with acetic acid, to a solution of calcium hypochlorite, gives a yellow precipitate, naphthylformylchloramine. It is easily soluble in chloroform, from which it is precipitated by ligroin. It is best recrystallized from hot ligroin (70° to 80°). The melting-point is 75°. It decomposes violently with an alcoholic solution of caustic potash.

0.1096 gram substance required 10.30 cc. N/10 thiosulphate.

	Calculated for $C_{11}H_8ONCl$.	Found.
Cl	17.25	17.26

β-Naphthylformylamine and Hypobromous Acid.—An alcoholic solution of formyl-*β*-naphthalide added to potassium hypobromite solution gave a yellow precipitate which, when crystallized from alcohol, melted at 164°. This compound was inactive toward potassium iodide, and on saponification, by heating an hour with 10 per cent potassium hydroxide, gave a flaky, white compound containing bromine, and melting at 61° when recrystallized from water and from alcohol. This is probably 1-brom-2-aminonaphthalene (m. p. 63°), and if so, it shows that the bromine atom migrates easily to the ortho position in the aromatic ring. This is the usual reaction with all halogen aryl amides when the para position is occupied.

Varying the conditions of precipitation gave unpromising gums composed of some active nitrogen bromide and other bromine derivatives of formylnaphthalide, and no further attempts were made to isolate the compounds.

Formyl-α-naphthalide also gave unsatisfactory results when attempts were made to brominate it. An alcoholic solution of the naphthalide added to hypobromite solution gave an active yellow precipitate, which, however, was so unstable that, on filtering, it instantly became hot and charred.

α-Naphthylacetylchloramine (*Acetylchloramino-α-naphthalene*), $C_{10}H_7NCl—CH_3CO$.—An alcoholic solution of acetyl-α-naphthalide with a little acetic acid added to an excess of calcium hypochlorite solution gives, after a few minutes, a precipitate of the chlorine compound. It can be recrystallized from hot ligroin in fine, pure white crystals, melting at 75°.

0.1150 gram substance required 10.24 cc. N/10 thiosulphate.

	Calculated for $C_{12}H_{10}NOCl$.	Found.
Cl	16.12	15.78

Halogen Derivatives of the Acyl Alkyl Amides.

Compounds of the type RCO—NHalR′, whether R is an alphyl or alkyl radical, are much more stable where R′ is an alkyl group than where it is an alphyl radical, because there is no tendency of the halogen atom to replace the hydrogen of an alkyl group as it does the hydrogen in an aromatic ring. It is possible, therefore, in such cases, and on trial it was found desirable, to attach chlorine to nitrogen by using the almost neutral solution made by dissolving chlorine in water instead of the usual alkaline calcium or sodium hypochlorite solution, or the acid solution obtained by acidifying these with weak acids such as acetic, carbonic, or boric. In this case, as in the others, hypochlorous acid is still doubtless the reagent effecting the change, for Jawkowkin[1] has shown that chlorine water contains hypochlorous acid as well as hydrochloric.

To determine whether chlorine acts directly on the amides or only when in aqueous solution and, therefore, presumably hydrolyzed, 1 gram of ethylbenzamide was dissolved in chloroform with a few drops of potassium hydroxide solution and a stream of chlorine passed in for some time. On evaporating the solvent, the unchanged ethylbenzamide was recovered with no trace of an active nitrogen chloride.

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[1] Ztschr. phys. Chem., **29**, 613 (1899).

Ethylbenzoylchloramine (*Benzoylchloraminoethane*), $C_6H_5CO—(NClC_2H_5)$.—Ethylbenzoylchloramine may be made in the usual way by using hypochlorite solutions, but the best results were obtained by dropping a saturated solution of ethylbenzamide in alcohol into about ten times its volume of chlorine water, which must not be too cold but at about 10°. The oily drops may be made to crystallize by adding a crystal of ethylbenzoylchloramine, or, if there is none at hand, by heating a little of the mixture until it crystallizes on cooling and shaking, and then adding this to the mixture. More chlorine water may be used to give another crop. The compound is soluble in ether, alcohol, and hot water, and may be crystallized from the last in the form of very fine, white needles. The melting-point is 53°.5.

0.1540 gram substance required 16.8 cc. N/10 thiosulphate.

	Calculated for $C_{18}H_{10}ONCl$.	Found.
Cl	19.31	19.37

The stability of the compound is quite remarkable. It is not decomposed by boiling water, and it melts without change. Warming with ammonia water reduces it rapidly.

The corresponding chlorine derivative of metanitrobenzamide is not so easily prepared. Ethylnitrobenzamide was made by the action of metanitrobenzoyl chloride on ethylamine hydrochloride in the presence of an alkali. It can be recrystallized from hot water and melts at 120°. Attempts to chlorinate this compound either by using hypochlorite solutions or chlorine water gave only traces of an active nitrogen halide.

Ethylbenzchloramide (1.8 grams) dissolved in alcohol was treated with potassium cyanide (0.7 gram). After warming for some time, the alcohol was distilled off, water added, and the solution extracted with ether. The ethereal solution gave only crystals of ethylbenzamide. On grinding together in a mortar ethylbenzoylchloramine (1.5 grams) with potassium cyanide (0.5 gram), the mixture became liquid and gave off a strong odor of hydrocyanic acid. In ten minutes the mass again became solid. It was extracted with ether which, on evaporation, gave crystals of ethylbenzamide, melting at 68° to 69°, so there were no other products in appreciable quantity. Therefore Berg's reaction does not take place under these conditions.

Ethylbenzoylchloramine (2 grams) was dissolved in dry ether, placed in the bottom of a tall cylinder filled with carbon dioxide, and a small glass bulb containing about 1 gram of zinc ethyl was dropped in. Although the solution was cooled to 0° the reaction was violent. On filtering and evaporating the solution, ethylbenzamide alone remained, having a melting-point of 66° without recrystallizing. There was, therefore, no evidence of any substitution of chlorine by ethyl.

Methylbenzoylchloramine (*Benzoylchloraminomethane*), $(C_6H_5CO)NClCH_3$.—Methylbenzoylchloramine may be made by dissolving methylbenzamide in alcohol, dilute acetic acid, or water, and adding the solution to a solution of calcium hypochlorite or sodium hypochlorite, or simply to chlorine water. A saturated aqueous solution of the amide with chlorine water, both ice-cold, was found to give the best results. As the compound is somewhat soluble, it is usually necessary to extract with ether. Methylbenzoylchloramine is a colorless oil, heavier than water. It does not solidify at a temperature of —16°, even when inoculated with a crystal of ethylbenzoylchloramine. This substance was tried because it, too, was difficult to solidify, and because it was thought that the two compounds might be isomorphous.

0.2035 gram substance required 23.15 cc. N/10 thiosulphate.

	Calculated for C_7H_8ONCl.	Found.
Cl	20.9	20.2

Methylbenzoylchloramine is decomposed by boiling with water or with dilute potassium hydroxide solution, by a strong solution of potassium hydroxide in the cold, by heating alone, and on long standing in a desiccator. Methylbenzamide is formed in all these cases and Beckmann's rearrangement does not take place. A sample containing 15.7 per cent chlorine was heated on a water-bath for half an hour, and was then found to contain 14.2 per cent active chlorine. Yet in some cases, on the evaporation of its ethereal solution by an air-blast, it decomposed spontaneously with the production of much heat. It cannot be distilled without decomposition, even in a vacuum. Concentrated hydrochloric acid attacks it, giving off chlorine. Ammonia water decomposes it slowly, even in the cold, regenerating the amide.

The difference in stability between this compound and the homologous ethylbenzoylchloramine is very marked and the reagents which decompose the former completely have but very little effect on the latter. Evidently the ethyl group exercises a protecting influence over the halogen which is attached to the same nitrogen, which may be due to stereochemical causes.

Amylacetamide.—Amylacetamide was prepared by slowly mixing an ethereal solution of isoamylamine (2 molecules) with an ethereal solution of the calculated quantity of acetyl chloride (1 molecule). After adding water to dissolve the amylamine hydrochloride, the ether was evaporated and then the amylacetamide distilled at a temperature of 230° to 232°. It is an oil and forms a pale-yellow platinum salt when chlorplatinic acid is mixed with its alcoholic solution and ether is added.

Amylacetylchloramine (*Acetylchlor 4-amino-2-methylbutane*), $CH_3CO—(NClC_5H_{11})$.—Adding isoamylacetamide to a solution of calcium hypochlorite gives the chlorine derivative as an oil, which, since it could not be distilled even in a vacuum nor solidified in a freezing mixture, could not be perfectly purified.

I. 0.3896 gram substance required 45.25 cc. N/10 thiosulphate.

II. 0.2552 gram substance required 30 cc. N/10 thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	Found. I.	II.
Cl	21.66	20.48	20.85

This compound is remarkably stable. It was not completely decomposed on standing two days in acid or in ammonia solution, nor on being warmed with these. Boiling water, however, decomposes it explosively. It is miscible with glacial acetic acid and is not decomposed by it in the cold. It can be dissolved in acetic acid and reprecipitated by the addition of an alkali.

Amylacetylchloramine having been prepared by the action of hypochlorous acid on amylacetamide, the method of introducing the chlorine and the acetyl group in the reversed order was tried by acetylating amylchloramine, in order to prove that in compounds of this class the halogen is really held by the nitrogen atom (see page 4). Isoamylchloramine was prepared in a way similar to that used by Berg.[1] Ten grams of the amylamine hydrochloride were dissolved in water and added to 50 cc. of sodium hypochlorite solution containing 8 per cent active chlorine. The oil separates at once and can be dissolved in ligroin (35° to 40°), washed with water, and the ligroin evaporated off in a vacuum-desiccator. A manometer is used to indicate when the ligroin is expelled. The chloramine is extremely unstable, and unless quickly purified, it goes over spontaneously, and sometimes instantaneously, into amylamine hydrochloride and the dichloramine.

0.1428 gram substance required 23.51 cc. N/10 thiosulphate.

	Calculated for $C_5H_{12}NCl$.	Found.
Cl	29.17	29.20

This amylchloramine was added to a little more than its volume of acetic anhydride. The two do not mix when cold, but on allowing them to reach room temperature reaction takes place, producing a slight rise in temperature. Glacial acetic acid was then added, and afterwards water. The amylacetylchloramine separated from the solution and could be washed with water, or could be dissolved with ligroin or ether and washed and obtained by evaporating off the solvent. The colorless oil appears identical in all respects with that obtained by chlorinating the amylacetamide, and although it was not obtained absolutely pure, as it could not be distilled in a vacuum nor solidified, the results are sufficiently close to identify it.

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[1] Bull. soc. chim., [3], 3, 687 (1890).

I. 0.3961 gram substance required 46.02 cc. N/10 thiosulphate.

II. 0.1079 gram substance required 12.93 cc. N/10 thiosulphate.

III. 0.1012 gram substance required 11.85 cc. N/10 thiosulphate.

	Calculated for $C_7H_{14}ONCl$.	Found. I.	 II.	 III.
Cl	21.66	20.60	21.25	20.80

Considering the ease with which the acetylation takes place and the low temperature, it is not probable that any rearrangement occurs, and the reaction therefore affords conclusive evidence in favor of the formula $CH_3CO—NClC_5H_{11}$ as representing the constitution of this compound, and in favor of the corresponding structure for its analogues.

The Chlor- and Bromimido Ethers.

Ethylchlorimidobenzoate and Potassium Cyanide.—Ethylchlorimidobenzoate[1] does not react with potassium cyanide in absolute alcohol even on heating, but if water is added the reaction takes place spontaneously, potassium chloride crystallizes out, and the imido ether is regenerated. Eighteen grams of ethyl chlorimidobenzoate in aqueous alcohol were heated on a water-bath with 8 grams of potassium cyanide for an hour. After pouring the mixture into water, extracting with ligroin, and distilling *in vacuo*, an oil was obtained which contained 9.15 per cent nitrogen.

0.1170 gram substance required 9.5 cc. N_2 at 23° and 739 mm.

	Calculated for $C_9H_{11}NO$.	Found.
N	9.41	9.15

The oil gave a slight reaction with potassium iodide and was therefore ethyl benzimido ether still containing a little of the unchanged chlorine compound. Berg's reaction does not, then, take place with the chlorimido ethers.

Ethyl chlorimidobenzoate and zinc ethyl give benzonitril as the chief product though a little ethylamine appears to be

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[1] Stieglitz: Am. Chem. J., 18, 755 (1896).

formed. Eight grams ethyl chlorimidobenzoate were dissolved in twice the volume of ether and added slowly to 5 grams of zinc ethyl, a reflux apparatus with a stream of carbon dioxide being used. The ether was distilled off and water added to the cooled residue. On acidifying the mixture with hydrochloric acid, a light oil separated which was extracted with ether and was proved to be benzonitril by dissolving it in alcohol with a little ammonium hydroxide and passing in hydrogen sulphide. The thiamide formed melted at 114°, and at 115° when mixed with some thiamide prepared from benzonitril for comparison. The benzonitril recovered weighed 4.2 grams, *i. e.*, 94 per cent of the theoretical yield.

The acid solution was made alkaline and distilled into hydrochloric acid in a Liebig bulb. On evaporation a very small amount of a salt was obtained which gave the isocyanide odor with caustic potash and chloroform. This showed the presence of a primary amine. An analysis of 0.0162 gram of the platinum salt gave 35 per cent Pt (calculated for $(C_2H_5NH_3)_2PtCl_6$, 39 per cent).

Ethyl Chlorimido-m-nitrobenzoate, *m*-$NO_2C_6H_4C(NCl)OC_2H_5$.—This compound is easily made by dropping the hydrochloride[1] of nitrobenzimido ethyl ester into an excess of sodium or calcium hypochlorite solution warmed to about 30°. On cooling, the chlorine compound becomes solid and can be picked off the surface with a spatula and recrystallized from warm alcohol or ligroin. It can be separated from any unchanged material by repeated extraction with ligroin.

0.2128 gram substance required 18.63 cc. N/10 thiosulphate.

	Calculated for $C_9H_9N_2OCl$.	Found.
N	15.50	15.52

It crystallizes in stellar groups of slender white needles and melts at 61° without decomposition, but when heated a little above this temperature it suddenly heats up and boils. On heating cautiously 5.5 grams of the compound, not absolutely dry, to the temperature required for decomposition, the chief

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[1] Lossen: Ann. Chem. (Liebig), **265**, 144 (1891); Tafel and Enoch: Ber. d. chem. Ges., **23**, 1550 (1890).

product was *m*-nitrobenzamide, with a small amount of ethyl *m*-nitrobenzoate. Both compounds were identified by mixing them with the synthetic preparations and taking the melting-points. No derivatives of nitraniline could be found.

It was thought that stereoisomers of this compound might be prepared, but all efforts to obtain these were in vain. For example, ethyl chlorimidonitrobenzoate was dissolved in ligroin and a very little dry hydrogen chloride passed in. The hydrochloride of nitrobenzimido ester was precipitated. Of the amount taken, 80 per cent was recovered.

Attempts were made to substitute the chlorine attached to the nitrogen atom of ethyl chlorimidonitrobenzoate by treating it with dimethylaniline with the hope of forming a derivative of *p*-aminodimethyl aniline,[1] but without success. The two compounds were heated together in alcohol, in strong oxalic acid solution, in dilute and in concentrated sulphuric acid, and without any solvent, but on testing the product in each case, after saponification in acid solution, with hydrogen sulphide and ferric chloride, there was no trace of methylene blue, and it must be concluded that dimethylphenylenediamine was not formed even in the minutest quantity. Treating the chlorine compound with α-naphthol and an alkali also gave no evidence of the substitution of chlorine by a radical.[1]

On heating the nitrobenzchlorimido ester in absolute alcohol it is not changed, but if a trace of water is present the benzoate is produced.

Nitrobenzchlorimido ester differs decidedly from the chloramides in being so stable. Alkalies do not cause the Beckmann rearrangement, nor even decompose it. Heating the ester for half an hour on the water-bath with an excess of 10 per cent potassium hydroxide does not affect it.

Ethyl Bromimido-m-nitrobenzoate, *m*-$NO_2C_6H_4C(NBr)OC_2H_5$.—The hydrochloride of nitrobenzimido ethyl ester is added to a cold solution of potassium hypobromite and the solution filtered at once. The precipitate is treated with ligroin, which dissolves the bromine compound and leaves the unchanged hydrochloride. By evaporation of the ligroin the bromimide

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[1] The apparently analogous chlorimides of quinone react in this way with anilines and phenols.

crystallizes out in fine white needles which melt at 71°, turn brown at 120°, and give off a gas at 130°.

0.0338 gram substance required 2.15 cc. N/10 thiosulphate.

	Calculated for $C_9H_9O_3N_2Br$.	Found.
Br	29.27	27.30

The substance melts under water without decomposition. Dilute hydrochloric acid gives off bromine, and ethyl nitrobenzoate is formed. As with the corresponding chlorine compound, the attempt to attach the nitrogen atom to a benzene ring was not successful. Heating the bromimide with dimethylaniline and then with concentrated and dilute sulphuric acid, and then treating with hydrogen sulphide and ferric chloride gave no methylene blue.

Ethyl Imidonitrobenzoate and Hypoiodous Acid.—Since the chlorine and bromine derivatives of *m*-nitrobenzimido ethyl ester were so stable, it was thought possible that the corresponding iodine derivative might be prepared in the same way. The imido ester was treated with iodine and then with a solution of potassium hydroxide and with crushed ice. In another experiment a hypoiodite solution, made by dissolving iodine in cold potassium hydroxide solution, was used, but although in all cases the ether or ligroin extract gave a minute residue of white or yellowish crystals from which dilute hydrochloric acid set free iodine, yet the desired iodine body was not definitely proved to exist, and it can probably be obtained, if at all, only from reagents when water is entirely excluded.

Ethyl Chlorimido-β-naphthoate, β-$C_{10}H_7C(NCl)OC_2H_5$.—The naphthimido ethyl ester was made by dissolving 15 grams of β-naphthonitril in 75 grams of ether and 8 grams of absolute alcohol, and passing in 10 grams of dry hydrogen chloride. The imido ester hydrochloride crystallizes out, on long standing, in plates. It decomposes with effervescence at 135° and forms the amide (m. p. 192°). Calcium hypochlorite solution has little effect on it in the cold, but if the solution is first heated to 60° or 70° the chlorine compound is readily formed, and can be filtered off on cooling and recrystallized from hot ligroin in beautiful stellar groups of needles and plates. It is very soluble in ether, from which it crystallizes in small, round nodules.

0.0525 gram substance required 4.48 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{12}ONCl$.	Found.
Cl	15.12	15.13

The chlorimidoester melts at 71° without decomposition, and only at 185° does it give off a gas with an agreeable odor, which burns with a green flame (ethyl chloride?). A gummy mass is left.

Ethyl chlorimido-β naphthoate is not decomposed even by boiling with strong ammonium hydroxide. With sodium methylate it reverts to the nitril. On heating 1.5 grams with 10 cc. of anhydrous methyl alcohol containing sodium methylate prepared from 0.3 gram sodium, it reacted at once, the imido ether melting and dissolving. On pouring the mixture into cold water, naphthonitril was precipitated. Recrystallized from ligroin it melted at 66°, even when mixed with naphthonitril.

Berg's reaction does not take place with naphthchlorimide ester. Five grams of imido ester with one gram of potassium cyanide in absolute alcohol were warmed for half an hour on the water-bath. Most of the alcohol was then distilled off and the residue extracted with ether. The part soluble in ether was distilled and found to be naphthonitril (m. p. 66°). The portion insoluble in ether (mostly potassium chloride) was dissolved in boiling water and some naphthoic acid crystallized out on cooling (m. p. 182°).

To 6 grams of the chlorimide in absolute ether were added 2.15 grams of zinc ethyl. There was no reaction at 0°, but when the mixture was allowed to come to the temperature of the room a slow effervescence began and continued for several hours. Filtering off the ether and evaporating it gave naphthonitril. On repeating the experiment with 20 grams of the chlorimide and 5.4 grams of zinc ethyl, there was a more rapid effervescence, but no precipitation of a zinc compound. On evaporating the solution in a vacuum, a salve-like mass was left which, treated with water, gave over 200 cc. of gas. The residue was extracted with ether and evaporated. A small portion of the product was recrystallized from ligroin and proved to be naphthonitril. In order to detect the presence of an amine, even in minute quantity, the remainder of the product was digested with sulphuric acid of varying concentration on a water-bath for several days. On pouring the solution into water, filtering off the unchanged nitril, making the filtrate alkaline with sodium hydroxide, and extracting it with ether, there was no evidence of an amine, from which it appears that zinc ethyl does not substitute ethyl for chlorine in acting on the chlorimide.

Ethyl Bromimido-β-Naphthoate, $\beta\text{-}C_{10}H_7C(NBr)OC_2H_5$.—This compound is made in the same way as the corresponding chlorine compound and resembles it in crystalline form and solubilities. Melting-point, 76°.5 to 77°.

0.1812 gram substance required 5.83 cc. N/10 thiosulphate.

	Calculated for $C_{13}H_{12}NOBr$.	Found.
Br	28.74	28.70

It crystallized from warm ligroin in pure white needles. It is remarkably stable. Boiling water and even sodium hydroxide solution attack it only very slowly. Standing over night with strong ammonium hydroxide does not decompose it.

To Professor Stieglitz, not only for his skill in directing this work but also for his patience and kindness toward me personally, I feel very grateful.