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MECHANISM OF THE VON BRAUN AMIDE DEGRADATIONS WITH CARBONYL BROMIDE OR PHOSPHORUS PENTABROMIDE

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Abstract—The isolation of the α-bromobenziminium hexafluoroantimonate **6**, the first intermediate in the amide degradation with carbonyl bromide, was previously announced. Present studies reveal that using either $COBr_2$ or PBr_5, the very first intermediate is the iminium tribromide (**7**). Reaction of the crystalline tribromide with cyclohexene gave the monobromide **8** nearly quantitatively and in crystalline form. Heating of the cyclic iminium monobromide **8** to 120° generates in high yield the α,ω-dihalogenoalkane (type **13**) and benzonitrile, while heating to 100° in bromobenzene allows isolation of the ω-bromoalkyl benzimidoyl bromide (**9** or **10**). An independent synthesis of this and other imidoyl bromides is elaborated. The equilibrium of imidoyl bromides with N-alkyl nitrilium bromides (**11**) can be shifted toward the nitrilium salt by dissolving in liquid sulfur dioxide or reacting with methyl fluorosulfate. All these steps have been monitored by NMR. The ω-bromoalkyl imidoyl bromide at 120° undergoes fragmentation *via* the nitrilium ion to an α,ω-dibromoalkane and benzonitrile. In addition to gaining mechanistic information (1) we achieved isolation of crystalline N-alkylene-α-bromoiminium bromides, and their smooth thermal decomposition, which makes the von Pechmann–von Braun type of degradation competitive to the Hofmann methylation; (2) a new procedure was found for preparing ammonium tribromides and iododibromides using carbonyl bromide; (3) a number of the heretofore unknown imidoyl bromides have been prepared and characterized, and their thermolysis and mass spectra studied.

INTRODUCTION

The conversion of N-monosubstituted amides into a nitrile and an alkyl chloride upon heating with phosphorus pentachloride and other reagents is well known.[1-4] N,N-Disubstituted benzamides under harsher conditions[5] were also dealkylated and the cyclic species[6] converted into an α,ω-dichloroalkane.[7] Replacing phosphorus pentachloride by pentabromide[3a] (or by a mixture[3b] of phosphorus trichloride and bromine) in the degradation of N-benzoylated piperidines allowed the use of somewhat lower temperatures. This one-step removal of nitrogen from a heterocycle, known as the von Braun reaction,[9] has found only limited applications,[10-12] mostly because of still drastic conditions, low yields and tarry by-products.

While the mechanism of the degradation of N-monoalkyl benzamides, *via* imidoyl chlorides,[3,4] has been extensively studied,[13-17] that of N,N-dialkyl and cyclic species was discussed only in one paper.[18] The authors elegantly proved that N-sec-butylbenzamide upon the action of phosphorus pentabromide give sec-butyl bromide with inversion of configuration, hence suggesting an S_N2 type displacement of the sec-butyl group. They also supposed a simultaneous attack of PBr_4^+ and Br^- upon N-benzoyl piperidine (**1**) leading to 5-bromoamyl-O-tetrabromophosphoryl benzimidoyl bromide (**2**) and subsequent fragmentation yielding benzonitrile, phosphoryl bromide and 1,5-dibromopentane. In the case of a more hindered carbon α to nitrogen Leonard postulated that the O-tetrabromophosphorylamide (type **2**) could be converted to the benzonitrilium salt (**3**), which then dissociates into an alkyl cation and benzonitrile. The fate of that cation would then depend on its environment, giving rise to either an olefin or an alkyl bromide.

This concept is in harmony with results on N-monosubstituted benzamides and benzimidoyl chlorides.[13-17] It also indicates, though not spelled out, that the von Braun reaction is a reversal of the Ritter reaction.[19]

RESULTS AND DISCUSSION

Our attention was focused on the von Braun reaction when the absolute configurations of the alkaloid sedridine[11] was correlated with S(+)2-octanol and that of (+)conhydrine[12] with R(−)3-octanol. The reaction of phosphorus pentabromide formed *in situ* with amides at 40–50° led to the isolation of phosphoryl bromide without any indication in the IR spectrum of benzonitrile formation.[20a] This fact was inconsistent with an all concerted

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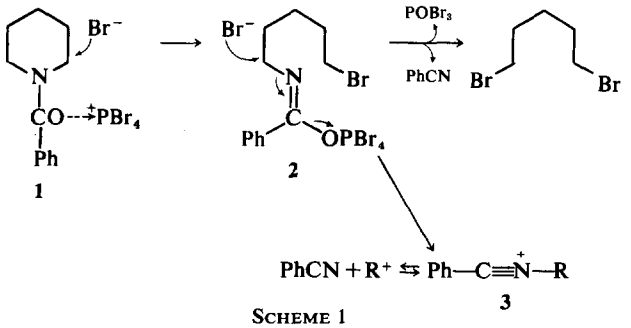


SCHEME 1

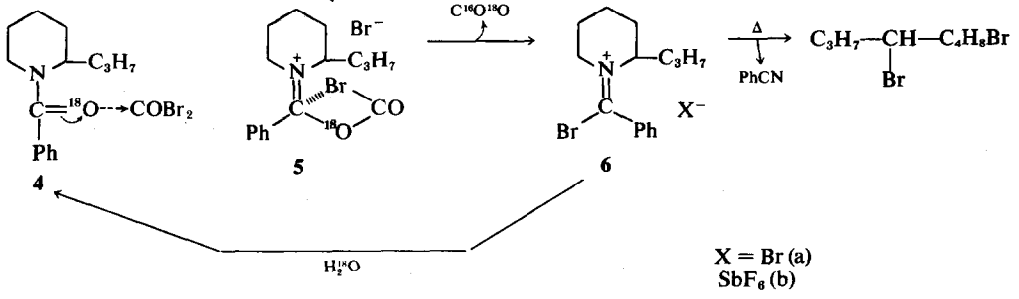
mechanism. Therefore, the explanation was offered[20b] that an α-bromobenziminium bromide (**6**) should be the first intermediate in the reaction. This was confirmed by reacting[21a] the less complex model N-benzoylconiine (**4**) with carbonyl bromide,[22] a novel reagent that leads to volatile by-products. Indeed, the crude N,N-1-propylpentamethylene-α-bromobenziminium bromide could be converted into the crystalline hexafluoroantimonate **6b** and the latter, after ion-exchange with bromide gave the expected von Braun products upon heating, i.e. benzonitrile and 1,5-dibromooctane.[21a] Furthermore, *racemic* 1,5-dibromooctane was obtained from optically active **4**, which indicated that, as with N-benzylacetamides, a carbonium ion might be involved in subsequent steps. One cannot preclude, however, that optically active 1,5-dibromooctane is racemized under the reaction conditions, e.g. by excess bromide ions.

Reaction of labeled benzoyl coniine (**4**; 60 atom % oxygen-18) with carbonyl bromide and subsequent analysis of the gaseous products in the mass spectrometer showed that carbon dioxide was produced with peaks at *m/e* 46 (55%) and *m/e* 44 (45%). This indicates that in the transition state **5** the carbonyl bromide carbon was attached to the amide oxygen in the form of an O-bromocarbonyl amide. It rules out any other transition states than 1:1 ratio of the reactants while not proving the 4-membered cyclic transition state versus attack by an external bromide ion as the next step.

Hydrolysis of the α-bromobenziminium bromide **6** with oxygen-18 labeled water gave benzoylconiine-oxygen-18 (**4**), thus iminium salt formation proved effectively reversible.

The next problem was to isolate the actual α-bromoiminium bromide in pure form and then delineate the intermediates between it and the von Braun products. An interionic reaction forming an ω-bromoalkylimidoyl bromide seemed likely which, in turn, would dissociate into a nitrilium salt to give von Braun products. In order to study imidoyl bromide formation we abandoned benzoylconiine because of the predictable complexity of a mixture of geometrical[21b] and optical isomers. Therefore, our next studies were performed with N-benzoylpiperidine and its symmetrically 2,6-disubstituted derivatives. Furthermore, carbonyl bromide, (b.p. 65°)[22] was used both as a solvent (instead of benzene) and as a reagent. Upon reaction of carbonyl bromide with N-benzoylpiperidine, N,N-pentamethylene α-bromobenziminium *tribromide* (**7** was isolated as orange colored crystals in quantitative yield. Treatment of the tribromide in acetonitrile with cyclohexene resulted in quantitative precipitation[23] of N,N-pentamethylene-α-bromobenziminium bromide (**8**) for the first time in crystalline form.

The formation of tribromide from monobromide salts with carbonyl bromide proved to be a general technique. A number of ammonium tribromides have been previously prepared[24] from the monobromides and bromine water. Near quantitative yields of a variety of quaternary ammonium tribromides and an iododibromide from quaternary



SCHEME 2

ammonium monobromides and iodides using carbonyl bromide with liberation of carbon monoxide have now been achieved.[23,25] This reaction deserves special attention, for phosgene does not undergo a similar process. The iminium tribromides that have been prepared from amides with carbonyl bromide are listed in Table 1. In carrying out the amide degradation tribromides need not be isolated if the reaction of the N,N-disubstituted amides with carbonyl bromide is carried out in cyclohexene as solvent. In this case the tribromide is converted *in situ* to the monobromide. Iminium tribromides and monobromides are characterized by the strong C=N band between 1578 and 1655 cm^{-1}. More important the α,α'-unsubstituted derivative shows in the NMR spectrum a pair of broad triplets between δ 3·87 and 4·54, separated by 0·2–0·4 ppm. The lower field signal was assigned to the methylene protons which, upon inspection of Catalin scale models, were close to bromine while the other two protons shielded by phenyl were at higher field. Similarly, the α-methine protons in α-substituted derivatives adjacent to bromine or to phenyl have different chemical shifts (for analytical data see Table 1 and for spectral data Table 2).

The bromoiminium bromide smoothly reacts with aniline to give N,N-pentamethylene-α-phenylbenzamidinium bromide. NMR showed no considerable shift of the α-CH_2 protons and IR gave no indication of an $=\overset{+}{N}H$ band, therefore, structure **8** (NHPh instead of Br) was postulated.

Monobromide **8** was easily converted in high vacuum at 120–130° into the von Braun products in 92% yield. This reaction was monitored by NMR in bromobenzene solution at 120° (Fig 1). The reaction is complete in 11 hr, (curves 1 and 3). The low field triplets of salt **8** disappear and a triplet integrating for the four protons of the CH_2Br in 1,5-dibromopentane appears, centered at δ 3·2 (neat δ 3·34). The iminium salt from N-benzoyl-2,6-dimethyl piperidine gave the von Braun products with 63% yield. This is three times greater[18] than in the classical procedure. It was thus revealed that the crucial point in obtaining high yields in the amide degradation with carbonyl bromide was the controlled preparation of the iminium bromide in pure form before decomposition. It is obvious that previously reported poor yields[11–13] in the von Braun reaction, when using a 1:1 molar ratio of phosphorus pentabromide to amide, were caused by the formation of a mixture of iminium tribromide and monobromide, which gave upon thermal decomposition impure, mostly overbrominated products. To overcome this, we used two moles of the phosphorus pentabromide to one mole of the benzamide to achieve complete tribromide formation, e.g. as observed in the case of N-benzoyl 2,6-dimethylpiperidine. Subsequently, the crude tribromide was converted by cyclohexene into the colorless pure monobromide. Also, in this way the convergence between amide degradations with carbonyl bromide and phosphorus pentabromide was proven.

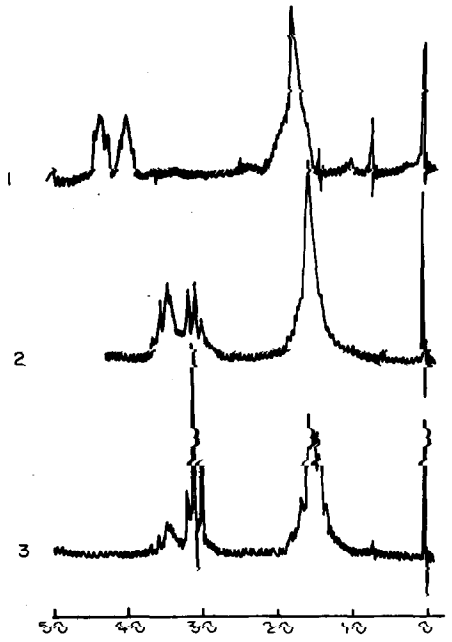


Fig 1. Thermolysis of iminium bromide **8**, followed by NMR. (1) N-Pentamethylenebenziminium bromide (**8**) in PhBr, before heating. (2) After heating 100°, 14 hr; integration shows 85% imidoyl bromide **9** and 15% 1,5-dibromopentane (**13**). (3) After heating iminium bromide **8** to 120° for 11 hr in PhBr; mostly pure **13** and benzonitrile.

Decomposition of N,N-pentamethylene-α-bromobenziminium bromide (**8**) to the imidoyl bromide **9** was carried out by heating **8** in bromobenzene at 100°, again monitored by NMR (Fig 1, curves 1 and 2). The methylene signals of the iminium bromide are shifted toward higher field as expected in the neutral imidoyl bromide, with close chemical shifts for $-CH_2-N=$ and $-CH_2Br$. methylbenziminium bromide[26] (**16**) at 98° in dibromomethane gave N-methylbenzimidoyl bromide (**14**, 75% yield) that could be purified by vacuum distillation. Here the chemical shift for the remaining NCH_3 protons is at δ 3·40, in contrast with the methyl shifts δ 3·97 and 4·21 in the salt **16** Attempted distillation of **9** at 10^{-3} mm/Hg, however, led to complete conversion to von Braun products. The crude N-5-bromopentylbenzimidoyl bromide (**9**) obtained from **8** was shown to be identical with an independently synthesized sample. A Gabriel-type synthesis was employed with 1,5-dibromopentane and potassium phthalimide giving a good yield of N-5-bromopentylphthalide. Hydrolysis with hydrobromic acid gave 5-bromopentylamine which was benzoylated under Schotten–Baumann conditions to N-5-bromopentylbenzamide. Treatment of the latter with phos-

Table 1. N,N-dialkyl and alkylene-α-bromobenziminium salts (type 7 and 8)

Type	N-substituents	Yield, %	M.p.[a] °C	Formula	Anal. Calcd, % C	H	Br	N	Found, % C	H	Br	N
7	Tetramethylene	100[b]	64	$C_{11}H_{13}Br_4N$	27·59	2·74	66·73		27·69	2·94	67·01	
7	Pentamethylene	100[b]	97	$C_{12}H_{15}Br_4N$	29·31	3·05	64·91		29·32	3·13	65·57	
7	1-Methylpentamethylene	100[b]	125	$C_{13}H_{17}Br_4N$	30·77	3·35	63·11		30·44	3·37	62·79	
7	1,5-Dimethylpentamethylene	98	124	$C_{14}H_{19}Br_4N$	32·24	3·65	61·42		32·27	3·75	61·50	
8	Dimethyl	90[B]	120 dec	$C_9H_{11}Br_2N$	36·89	3·78		4·78	36·54	4·06		4·50
8	Tetramethylene	100[A], 93[B]	178 dec	$C_{11}H_{13}Br_2N$	41·41	4·11	50·09		40·02	4·04	49·36	
8	Pentamethylene	100[A], 95[B], 94[C]	195 dec	$C_{12}H_{15}Br_2N$	43·24	4·50	47·99		42·99	4·41	47·95	
8	Dimethyl-α-bromoformiminium[c]	89[B], 95[C]	164[h] dec	$C_9H_{11}Br_2N$								
8	1-Methylpentamethylene[d]	93[A]	160[d]	$C_{13}H_{17}Br_2HgBr_2$	22·06	2·40	45·27		21·95	2·31	45·70	
8	1,5-Dimethylpentamethylene	90[B]	amorphous	$C_{14}H_{19}Br_2N$	46·54	5·26	44·33		spectral data only			
8	1-n-Propylpentamethylene[f]	85[A], 25[D]	85–95[i]	$C_{15}H_{21}BrNSbF_6$	33·93	3·99	15·05	2·64	34·25	3·92	15·80	2·63

[a]In a sealed tube. [b]Yields of tribromides have been calculated upon the amides. [c]Formyl group instead of phenyl. [d]Analyzed as the tribromomercurate. [e]Extremely hygroscopic, hence it was analyzed as the tribromide and thermolyzed without crystallization. [f]Hexafluoroantimonate. [g]Prepared with carbonyl bromide in cyclohexene. [h]Lit.[44] 156–158°. [i]Sublimed at 62°/10^{-2} mm. [j]Geometrical isomers. [A]From tribromide made with cyclohexene. [B]Using PBr_5 and cyclohexene, without separation of the tribromide. [C]Carbonyl bromide in cyclohexene. [D]Carbonyl bromide in benzene.

Table 2. N,N-dialkyl and alkylene bromobenziminium tribromides (Type 7) and bromides (type 8) pertinent IR and NMR spectral data

Type	N-Substituents	IR (KBr) cm^{-1} $\overset{+}{C{=}N}$	NMR δ $\overset{+}{N}{-}CH$	$\overset{+}{N}{-}CH_2$	$\overset{+}{N}{-}CH_3$	$\overset{+}{N}{-}\underset{\vert}{C}{-}CH_3$	β,γ CH_2	Aryl	Other Signals
7	Tetramethylene[c]	1620		4·08[a] (t, J = 6 Hz) 4·30 (t, J = 6 Hz)			2·16–2·45 (m)	7·73 (s)	
7	Pentamethylene[c]	1595		4·13 (t)[a,i] 4·54 (t)			2·00–2·10 (m)	7·78 (m)	
7	1-Methylpentamethylene[b]	1585	5·52 (m)	5·04[a] (d, J = 13 Hz) 4·05–4·50 (m)		1·68 (d)[a] 1·79 (d)	1·70–2·35 (m)	7·72 (s)	
7	1,5-Dimethylpentamethylene[c]	1578	4·85 (m)[a] 5·32 (m)			1·46[a] (d, J = 7 Hz) 1·73 (d, J = 7 Hz)	1·97–2·10 (m)	7·70 (s) 7·53 (m)	
8	Dimethyl[d]	1640[f]			3·97 (s)[a] 4·21 (s)			7·97 (m)	
8	Tetramethylene[e]	1655,[f] 1600		3·87[a] (t, J = 6·5 Hz) 4·05 (t, J = 6·5 Hz)			2·03–2·40 (m)	7·72 (s)	
8	Pentamethylene[e]	1615[f]		4·32 (t, J = 6 Hz) 4·68 (t, J = 6 Hz)			1·90–2·44 (m)	7·72 (s)	
	1-Methylpentamethylene[b,g]	1585[f]	5·50 (m)[a] 4·95 (m)			1·66 (d)[a] 1·87 (d)	1·90–2·20 (m)	7·75 (s)	
	1-n-Propylpentamethylene[c,h]	1595	5·25 (m)[a] major 5·00 (m) minor	4·00 (m)			1·50–2·50	7·70 (m)	$H_2C{-}CH_3$, 1·15 (t)

[a] Lower field signals were ascribed to protons close to bromine; higher field signals to those close to phenyl. [b] NMR spectra in CD_3NO_2. [c] NMR in CD_3CN. [d] NMR in $CDCl_3$. [e] NMR in CF_3CO_2H. [f] Mull. [g] Tribromomercurate. [h] Hexafluoroantimonate. [i] Chemical shifts in $CDCl_3$ were 4·40(t) and 4·75(t).

phorus pentabromide gave the amorphous tribromide which upon addition of cyclohexene gave the crystalline hydrobromide, which upon mild heating in benzene, lost hydrogen bromide to give imidoyl bromide **9**.

No simple imidoyl bromides have been heretofore described while a large number of chlorides[3,27] and fluorides[3,4] as well as some hydrazidoyl and amidinoyl bromides[3] are known. The new technique, *via* the imidoyl bromide hydrobromide without isolating the tribromides proved applicable to a number of compounds (Tables 3 and 4).

Benzimidoyl bromides (Type **10**) play an important role in our scheme* (Scheme 3) as labile intermediates which dissociate to alkyl nitrilium salts (**11**) followed by fragmentation upon heating to **12** and **13**. Heating of imidoyl bromide **9** to 120° neat or in bromobenzene for 1·5 hr was also monitored by NMR. As seen in Fig 2, after 3 hr the lower field signal δ 3·63 in curve 1 (=N—CH_2) disappears in curve 2 while the triplet for CH_2Br at δ 3·34 of **9** now integrates for four protons, as expected for 1,5-dibromooctane **13**.

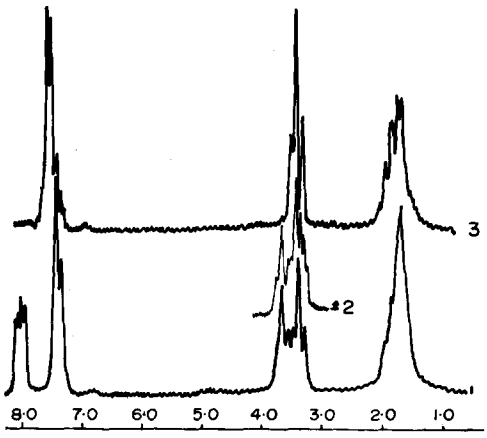
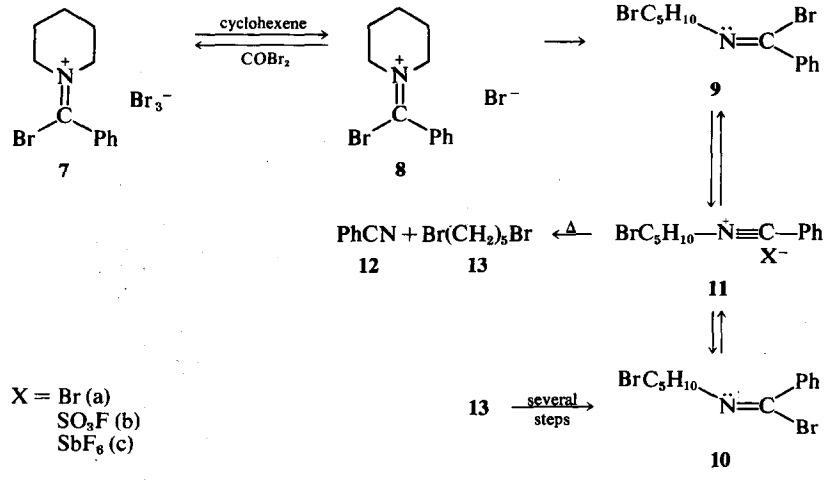


Fig 2. Thermolysis of imidoyl bromide **9** and **10**, monitored by NMR. (1) Imidoyl bromide, neat, before heating. (2) After heating to 125°, 30 min, neat. (3) After heating for 1·5 hr, (neat). Practically pure 1,5-dibromopentane plus benzonitrile.



SCHEME 3

No indication for the existence of geometrical isomers at the C=N bond was found in the NMR spectrum of N-methylbenzimidoyl bromide (**14**) at −85°, in toluene-d_8. This may be due to preferential formation of one of the isomers, a rapid *syn-anti* interconversion, or coincidental overlap of the chemical shifts of both isomers. Interestingly, *syn-anti* isomers of imidoyl fluorides, but not of chlorides, have been isolated.[4] However, Olah *et al*[28] have shown by NMR that the N-methyl singlet in N-methylbenzimidoyl chloride became a doublet at −50° in SO_2, which is indicative of stereomutation, probably *via* equilibration with the nitrilium salt. Since stereomutation around a C=N bond requires usually about 20 kcal/mole energy of activation for N-alkyl derivatives,[29] and also considering Olah's results, one reasonable explanation is a rapid dissociation of one of the geometrically isomeric imidoyl bromides **9** into the nitrilium bromides (Type **11**) and recombination of the ions into either the *syn*

*Circumstantial evidence for their formation as by-products, besides 4,8-dibromo-2-octylbenzoate, was mentioned in the von Braun reaction of N,O-dibenzoylsedridine,[12] for the higher boiling fraction gave 8-benzamido-4-bromo-2-octylbenzoate upon hydrolysis. Similarly, with N,O-dibenzoylconhydrine, 8-bromo-4-benzamido-3-octylbenzoate was obtained.[13] Based on our recent experience these products had to be formed during thermolysis of the α-bromobenziminium bromides from the intermediate imidoyl bromides by the action of moisture. Thus these facts also fit well in with the present mechanistic picture.

Table 3. Benzimidoyl bromides and their hydrobromides (type 9)

N-Substituent	Yield, %	M.p.[d] °C	B.p. °C (mm/Hg)	Formula	Anal. Calcd, % C	H	Br	N	Found, % C	H	Br	N
Methyl	88·5[a]		73–74 (1·0)	C_8H_8BrN	48·51	4·06		7·07	48·33	4·25		6·86
Hydrobromide	86[b]	133–136[d]	60[c] (0·20)	$C_8H_9Br_2N$	34·44	3·25	57·29	5·02	34·50	3·41	57·34	5·09
Ethyl	84[a]		54–55 (0·1)	$C_9H_{10}BrN$	50·96[f]	4·75		6·61	50·28[f]	4·42		6·43
Hydrobromide	84[b]	148–152[d]	55[c] (0·20)	$C_9H_{11}Br_2N$	36·89	3·78	54·50[f]		37·35	3·95	53·64[f]	
n-Butyl Hydrobromide	51·5[b]	110–112[d]	25[c] (0·025)	$C_{11}H_{15}Br_2N$	41·15	4·71		4·36	41·34	5·00		4·22
N-5-Bromopentyl	92[a]		120–125[e] (0·01)	$C_{12}H_{15}Br_2N$	43·24	4·51	47·99		43·13	5·11	46·93	
Hydrobromide	58·5[b]	106–108	50[c] (0·15)	$C_{12}H_{16}Br_3N$	34·81	3·90		3·38	35·19	3·70		3·15

[a]Yields of imidoyl bromides were calculated upon the hydrobromides. The hydrobromides suspended in benzene gave upon short heating the bases. [b]Yield relative to the benzamide. [c]Sublimation *in vacuo*. [d]All hydrobromides melt with decomposition. [e]Decomposed on distillation to benzonitrile and 1,5-dibromopentane. [f]Discrepancies may be caused by sensitivity of those compounds to heat and/or moisture.

Table 4. IR and NMR data on N-alkylbenzimidoyl bromides and of their hydrobromides

N-Substituent	IR (NaCl) cm^{-1} $>C=N-$ and $>C=\overset{+}{N}<_{H}$	NMR, δ $=N-CH_2$	$=\overset{+}{N}HCH_2$	$=N-CH_3$	$=\overset{+}{N}H-CH_3$	Remote CH_3 and CH_3	Aryl and Other Signals
Methyl-	1675 (vs)	—	—	3·40 (s)	—	—	7·30 (m) 7·95 (m)
-hydrobromide[a]	2500 (vs) 1635 (vs)	—	—	—	3·78 (s)	—	7·66 (m) 8·43 (m) NH 14·03 (s)
Ethyl	1672 (vs)	3·65 (q) $J = 7$ Hz	—	—	—	1·32 (t) $J = 7$ Hz	7·31 (m) 7·95 (m)
-hydrobromide[a]	2500 (vs)	—	4·23 (q) $J = 7$ Hz	—	—	1·60 (t) $J = 7$ Hz	7·66 (m) 8·41 (m) NH 14·57 (s)
n-Butyl, hydrobromide	2500 (vs) 1630 (vs)	—	4·17 (t) $J = 6$ Hz	—	—	1·70 (m) 1·02 (t) $J = 6$ Hz	7·66 (m) 8·43 (m) NH, 14·57 (s)
n-5-Bromopentyl[b]	1670 (vs)	3·60 (t) $J = 6·5$ Hz	—	—	—	2·0 (m)	3·34 (t, $J = 6·5$ Hz) CH_2Br, partly overlapped by $N=CH_2$
-hydrobromide	2450 (vs) 1630 (vs)	—	4·19 (t) $J = 6·0$ Hz	—	—	1·90 (m)	7·70, 8·43 (m) 3·44 (t, $J = 6$ Hz) CH_2Br 4·19 (t, $J = 6$ Hz) CH_2N

[a]Mull. [b]Prepared from 5-bromopentylbenzamide with $COBr_2$ or PBr_5 *via* its hydrobromide, also *via* thermal neutralization in bromobenzene of benziminium bromide 7.

or *anti* configurations (**9** or **10**). This has been investigated by low temperature NMR, but unfortunately with no success. However, we found that N-methylbenzimidoyl bromide (**14**) dissolved in liquid SO_2 gave the same NMR spectrum as N-methyl benzonitrilium fluorosulfate (**15**; X = OSO_2F), which shows that complete dissociation of the imidoyl bromide **14** took place (Fig 3). In acetonitrile-d_3 **14** and **15** show very different chemical shifts (Fig 4).

Another approach, using bromine-82, to the problem of determining the rate of the exchange of bromide in the imidoyl bromide with external bromide is in progress. A high rate of exchange would indicate either rapid dissociation and association, or alternatively a very rapid addition and elimination of bromine on the C=N bond; the first explanation is more in line with kinetics observed in the hydrolysis[30] of imidoyl chlorides. There is a further observation concerning facile conversion of imidoyl bromides into nitrilium salts which corroborates the former view. N-Methylbenzimidoyl bromide (**14**), when treated with methyl fluorsulfate ("magic methyl"),[31] gave rise to only 20% N-

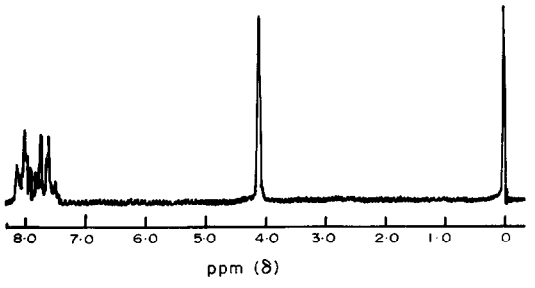


Fig 3. NMR spectrum of N-methylbenzimidoyl bromide and of N-methylbenzonitrilium fluorosulfate in liquid SO_2 at − 29°.

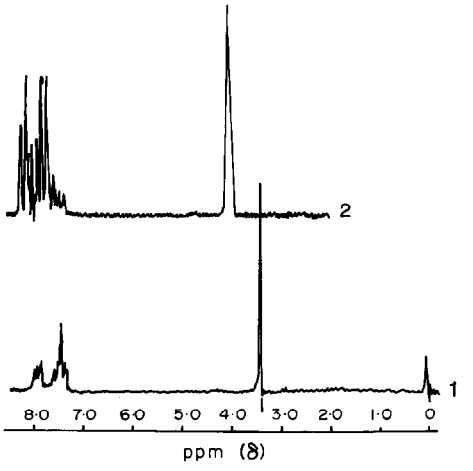
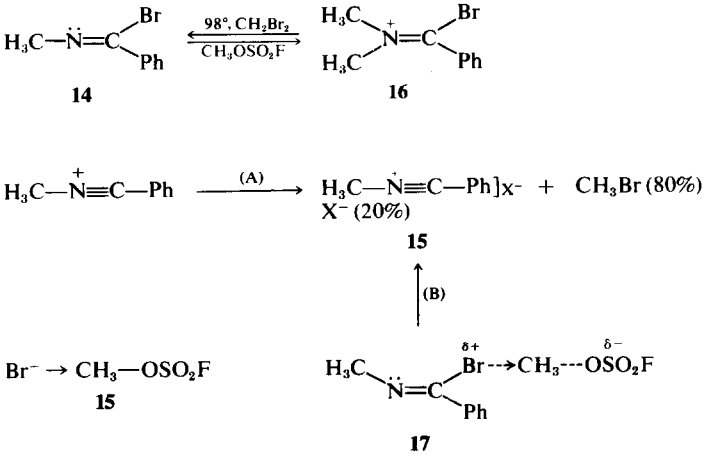


Fig 4. NMR spectrum of N-methylbenzimidoyl bromide and of N-methyl benzonitrilium fluorosulfate in acetonitrile-d_3 at 25°.

methylbenzonitrilium fluorosulfate (**15**; X = OSO_2F) and an equivalent amount of methyl bromide. Similarly N-5-bromopentylbenzimidoyl bromide (**9** or **10**) with magic methyl gave quantitatively N-5-bromopentylbenzonitrilium fluorosulfate (**11**, X = FSO_3^-) as shown by NMR spectra taken before, 5 min, and 15 min after addition of magic methyl (Fig 5 and Table 5).

This novel reaction, i.e. methylation of bromide in preference to N-methylation, can be explained by assuming that the imidoyl bromide is in equilibrium with the alkylnitrilium bromide; the bromide ion is rapidly methylated and the equilibrium shifted toward the nitrilium ion (Pathway A). Alternatively, direct methylation by magic methyl of the bromine atom in the imidoyl bromide cannot be ruled out. The dialkyl bromoiminium ion type transition state (**17**) would then break down to give



SCHEME 4

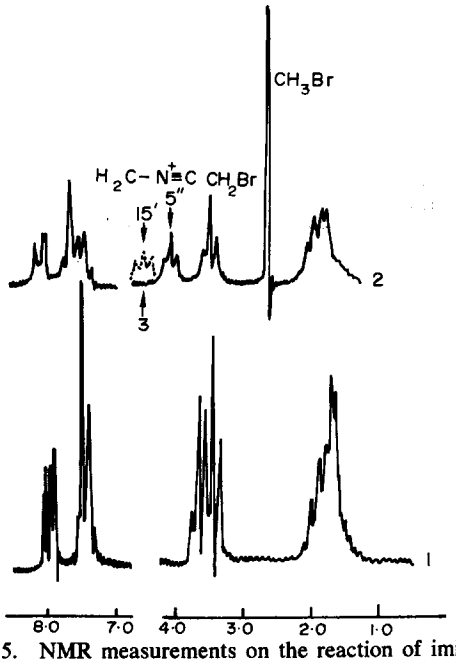


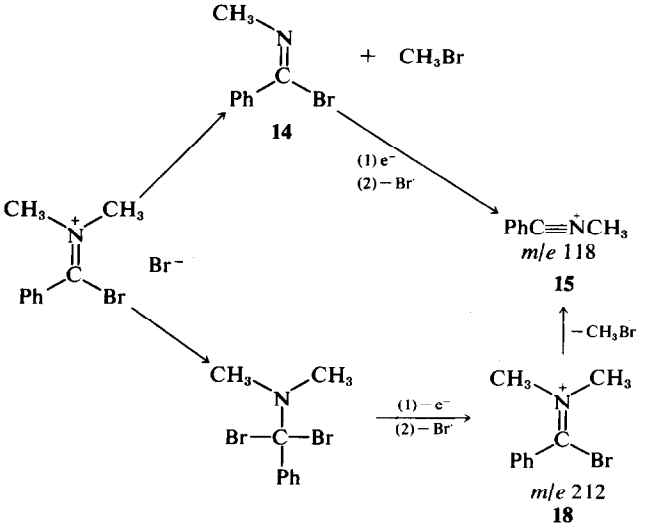
Fig 5. NMR measurements on the reaction of imidoyl bromide **9** with Magic Methyl in acetonitrile-d_3.
(1) 5-Bromopentylbenzimidoyl bromide **9**.
(2) Spectrum 5 min after Magic Methyl was added.
(3) Methylene protons α to nitrogen 15 min after addition of Magic Methyl.

methyl bromide and the nitrilium fluorosulfate (Pathway B). Dialkylbromonium hexafluoroantimonates have recently been synthesized[32] but the fluorosulfates have not.

N-Methylbenzonitrilium fluorosulfate was reconverted by lithium bromide into the imidoyl bromide showing that the dissociation process is reversible. Similarly, N-5-bromopentylbenzonitrilium fluorosulfate, prepared from the imidoyl bromide **9** and magic methyl, regenerated the imidoyl bromide in a few minutes when lithium bromide was added.

This indicates that nucleophiles react primarily on the nitrilium carbon and not on the aliphatic carbon alpha to nitrogen. Therefore, the last step of the fragmentation at the nitrilium bromide into von Braun products very likely proceeds *via* dissociation into an alkyl cation and benzonitrile and not by way of a concerted nucleophilic attack of bromide upon the aliphatic α-carbon.

An insight into the fragmentation pattern of iminium and of imidoyl bromides was supplied by a mass spectral study by two of us with Smith.[33] Heating of non-volatile salts in the inlet of a mass spectrometer first leads to the formation of neutral species which are then vaporized and give rise to the observed spectrum.[34] Thus, thermal neutralization of N,N-dimethyl-α-bromobenziminium bromide (**18**) at 140° in the mass spectrometer occurs in two ways (Scheme 5), one of which might be identical with the simple chemical fragmentation process. Nucleophilic dealkylation, a commonly observed phenomenon in the mass spectra of ammonium salts,[34] leads to methyl bromide and N-methylbenzimidoyl bromide (**14**) which does not give rise to a molecular ion. However, "synthetic" N-methylbenzimidoyl bromide generates ions identical to those found in the spectrum of the bromoiminium bromide **18**, the major process being loss of a bromine atom giving the N-methyl nitrilium ion **15**, which is only stable in the mass spectrometer. Alternatively, attack by bromide on the sp^2 carbon bonded to nitrogen may generate N-(α,α-dibromo)benzyldimethylamine (**19**) (Scheme 5). Volatilization of **19** is followed by ionization and loss of a bromine atom to give the ion **18** at *m/e* 212. This ion then loses methyl bromide, as indi-



SCHEME 5

Table 5. Some data of the benzimidoyl halide-magic methyl reaction

N-Alkylbenzimidoyl halide	Product, NMR, δ							
	NMR		N-Methyl α-Halobenziminium salt			Benzonitrilium salt		
	$=N-CH_3$	$=N-CH_2$	Yield %	$=\overset{+}{N}(-)-CH_3$	$=\overset{+}{N}-CH_2$	Yield %	$\equiv\overset{+}{N}-CH_3$	$\equiv\overset{+}{N}-CH_2$
N-Methyl-chloride	3·40	—	33[+]	4·01[a], 3·83[b]	—	67	4·21	—
N-Methyl-bromide	3·40	—	17[+]	4·04[a], 3·79[b]	—	83	4·10	—
N-5-Bromopentyl-bromide	—	3·66[c]	0	—	—	100	—	4·44

[a]Methyl, syn to halogen. [b]Methyl, anti to halogen. [c]Signal moves upon addition of Magic Methyl in 20 min completely to δ 4·44.

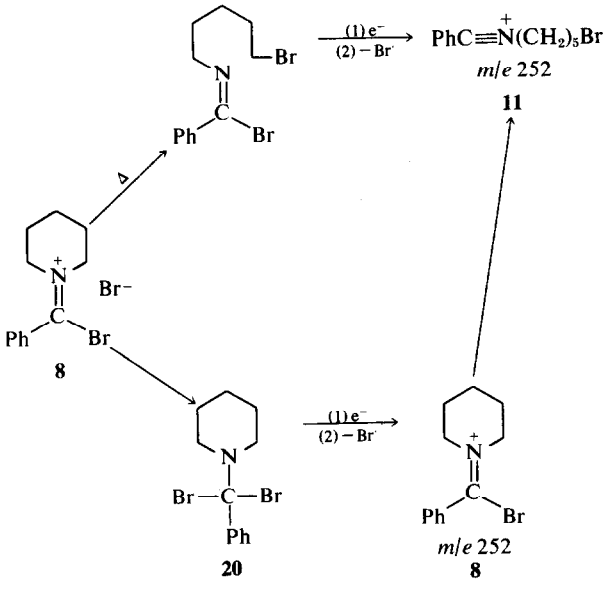
Table 6. Physical and spectral data of N-benzoylated amines

N-Benzoyl-	Yield, %	M.p.°	IR (melt) C—O, cm^{-1}	$N-CH_2$	N—CH	NMR, δ, ($CDCl_3$) Remote CH_2 and CH_3	Aromatic and Other Protons
Pyrrolidine	71.6	45–47[37]	1615 (s)	3.37 (t, J = 7 Hz) 3.60 (t, J = 7 Hz)	— —	1.70–2.05	7.42 (m)
Piperidine	79.3	46.5–49[37]	1635 (s)	—		1.60	7.35 (s)
2-Methylpiperidine	68.0	47–49[35]	1630 (vs)	2.97 (m, ax)	4.53 (m)	1.78 (d, J = 6.5 Hz) 1.58 (broad s)	7.33 (s)
2,6-Dimethylpiperidine	87.0	110–112[36]	1620 (vs)	—	4.30 4.64 (m)	1.63 (broad s) 1.27 (d, J = 6 Hz)	7.37 (s)
2-n-Propylpiperidine	95.0	Bp 125[11b] (0.02 mm)	1630 (vs)	2.90 (m)	4.80	1.6 (m) 0.90 (t)	7.40 (m)
n-Butylamine	90.5	41–42[38]	1640 (vs)	3.41 (g, J = 6.5 Hz)		0.93 (t, J = 6.5 Hz) 1.47 (m)	6.75 (m, NH)

cated by the appropriate metastable peaks (obsd. 65·5 broad, calcd. 65·0 and 65·7), to contribute to the intensity of N-methylbenzonitrilium ion (**15**).

N,N-Pentamethylene-α-bromobenziminium bromide (**8**) similarly may generate either 5-bromopentylbenzimidoyl bromide (**9**) or N-(α,α-dibromo)benzylpiperidine (**20**) when heated to 300° in the mass spectrometer. The ionization and subsequent loss of a bromine atom from **20** would give an ion at *m/e* 252, probably **8**, indistinguishable from the N-5-bromopentylnitrilium ion **11**.

Our present scheme on the mechanism assumes two sequential displacement reactions. The first is the nucleophilic dealkylation of a α-bromobenziminium bromide (Type **8**) forming the benzimidoyl bromide (Type **9**, **10**), while the second involves the fragmentation of the alkylnitrilium bromide (Type **13**) into von Braun products. The stereochemistry of this second step has been well studied by Leonard.[18] He showed that with sec-butylamide, as we now would interpret, there was an inversion[17] of configuration at the N-sec-butylbenzimidoyl bromide ⇆ N-sec-butylbenzonitrilium bromide stage. Mohan[15] on the other hand showed that some benzylic type amides with carbonium ion stabilization at the fragmentation stage showed racemization. The steric course of the first dealkylation step, that of N,N-disubstituted iminium salts, however, so far lacks direct support.*



EXPERIMENTAL

General. All b.p's and m.p's are uncorrected; m.p's were taken with the Electrothermal Model 1A 6304 apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, by Chemalytics, Inc., Tempe, Arizona, and some by Dr. F. Pascher, Bonn, Germany.

IR spectra were recorded on a Beckmann IR-4, IR-8 or a Perkin-Elmer Model 137 Spectrophotometer, mostly in KBr, some in Nujol or Fluorocarbon mull. The abbreviations used to describe the intensities of the IR peaks are as follows: vs = very stong, s = strong, m = medium, and w = weak. NMR spectra were obtained from a Varian Model HA-60, A-60 or T-60 Spectrometer using 10–15% (w/v) solns with TMS as an internal standard. The multiplicities of the NMR signals are abbreviated in the text as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Most of the mass spectra were recorded on a Nuclide 12-90-G instrument, operated at 70 eV ionizing energy, some with a Varian M-66 model. A heated direct-inlet was used for the bromoiminium salts. Carbon dioxide-oxygen[18] was analyzed at the Research Center of the Canadian Army in Valcartier, Quebec.

Gas chromatography was carried out on a Model 6500 Carle Thermal Conductivity Basic Chromatograph.

Most of the preparations and reactions of iminium and imidoyl bromides were carried out in a Hydrovoid Atmosphere Control System.

Most of the reagents and starting materials were commercial samples. ^{18}O-Benzoyl chloride was supplied by the National Research Council of Canada, by Dr. L. Leitch.

*Assuming that in the thermal interionic reaction[21a] of (−) N,N-1-propylpentamethylene α-bromobenziminium bromide (**6a**) there was preference of bromide attack on the primary rather than on the chiral C-2 carbon, the major product should be nonracemic N-(1-bromo-5-octyl)- benzimidoyl bromide (Type **10**) involving no major stereochemical change. Since the final product of its thermal decomposition *was* racemic 1,5-dibromooctane, most probably racemization occurred during fragmentation of N(1-bromo-5-octyl)-benzonitrilium bromide. The complicating factor is that racemization of the sec-alkyl bromide under thermal conditions by excess bromide ion cannot be ruled out.

Preparations

Carbonyl bromide. A 500 ml 2-necked flask, equipped with a dropping funnel and condenser, was heated in an oil bath to 125–130°. Finely ground CBr_4 (100 g, 0·30 mol) was added quickly and, upon melting, was vigorously stirred. The dropwise addition of conc H_2SO_4 (90 ml, 166 g, 1·68 mol) was immediately started. Preheating the flask and grinding the CBr_4 prevents considerable sublimation of CBr_4 before complete melting and the start of H_2SO_4 addition. The addition of H_2SO_4 takes *ca* 2·5 hr, however, after 15 min, a dark brown liquid (mixture of carbonyl bromide and bromine) distilled at 60–70° and was collected in a receiver at 0° at avoid loss of carbonyl bromide. The reaction was complete after 3·5–4 hr and 47·9 g of crude distillate was collected.

The distillate was transferred to a 100 ml 3-necked flask equipped with a nitrogen inlet bubbler and an outlet that passed through a reflux condenser. Ethylene was then bubbled slowly (*ca.* 20 ml/min) through the mixture with simultaneous stirring. The flask was cooled with ice and the reflux condenser prevented the ethylene from carrying away any carbonyl bromide. The absorption of Br_2 by ethylene takes *ca* 3 hr and results in a colorless mixture of carbonyl bromide and 1,2-dibromoethane (b.p. 131°). Distillation of this mixture gave 38·5 g (68%) of carbonyl bromide, b.p. 65–67°; von Bartal reports[22] b.p. 64–65°. Again the receiver must be cooled to prevent loss of the volatile product.

Since carbonyl bromide is extremely poisonous and also sensitive to light, this preparation was carried out in a good hood with the reaction vessels used, whenever possible, being protected from light with black tape. Also the doors of the hood were covered with aluminum foil and kept closed whenever possible. Carbonyl bromide was never handled outside of the hood and was stored in a tightly sealed container at −10° in the freezing compartment of a refrigerator. Upon standing, this reagent darkens to a deep red due to formation of molecular Br_2. Also upon long standing considerable pressure will build up in the sealed container due to the photochemical decomposition of carbonyl bromide to Br_2 and CO, and it is advisible to release this pressure at least every week. It was found that carbonyl bromide could be conveniently purified immediately before use by shaking with metallic mercury[22] and either decanting or distilling the colorless supernatant liquid.

IR: NaCl (neat) 1805 (vs, C=O), 775 (s), 780 (s) 720 (vs, C—Br) cm^{-1}.

General procedure for the preparation of N*-benzoylated amines.* A Schotten–Baumann procedure was employed for the synthesis of the amides used in this work. To 1·0 mole of amine and 1·3 mole of NaOH in 400 ml water, 1·0 mole benzoyl chloride was added over 1·5 hr. The mixture was maintained at 35–40° and stirred vigorously. After a reaction time of 2–2·5 hr the resulting organic layer was separated and washed twice with 25 ml of 10% NaOH and then 4 times with 25 ml of water. The organic layer was dissolved in benzene and dried over Na_2SO_4. Evaporation of the solvent gave the N-benzoylated amine.

Physical and spectra data of the amides prepared are summarized in Table 6.

Preparation of α-bromobenziminium tribromides with carbonyl bromide. N-Benzoylpiperidine (1·9 g, 0·01 mol) was placed in a 50 ml 3-necked flask equipped with a septum and a N_2 inlet with the outlet passing through a reflux condenser and then through a $Ba(OH)_2$ aq. The system was flushed with dry N_2 for 0·5 hr before use. Carbonyl bromide (5·6 g, 0·03 mol) was added slowly by syringe in three equal portions while the flask was cooled with ice. The soln immediately became deep red with vigorous evolution of CO_2. A small positive pressure of N_2 was maintained throughout the reaction and the CO_2 liberated was trapped quantitatively as $BaCO_3$ in the $Ba(OH)_2$ aq. The reflux condenser prevented any loss of the volatile carbonyl bromide. The reaction mixture was stirred until no further gas was evolved, approximately 3 min. The addition of dry ether (10 ml) caused the quantitative precipitation (4·9 g) of the analytically pure orange–red colored **7**, m.p. 94–97° (sealed tube). A similar technique was used for the other bromoiminium salts.

The analytical data and physical properties of N,N-pentamethylene-α-bromobenziminium tribromide and other tribromides that were prepared by a similar procedure are found in Table 1. IR and NMR data are given in Table 2.

Preparation of α-bromobenziminium tribromides with phosphorus pentabromide. 2,6-Dimethyl-N-benzoylpiperidine (3·0 g, 0·014 mol) was placed in a 50 ml 3-necked flask equipped with a septum and a N_2 inlet that was connected to a pressure release through a gas bubbler. Benzene (20 ml) was introduced and the system flused with N_2 for 30 min. PBr_3 (4·6 g, 0·017 mol) was added by syringe followed by 4·5 g (0·028 mol) of Br_2. The mixture was stirred for 1 hr during which time a red oil precipitated. The supernatant was removed and the oil washed first with 10 ml benzene and then with dry ether (15 ml). Washing caused the red oil to solidify and the orange-red colored N,N-1,5-dimethylpentamethylene-α-bromobenziminium tribromide (7·0 g, 97·6%) was collected in the dry box. Recrystallization from chloroform gave 6·3 g (88%) of the tribromide, m.p. 124–127° (sealed tube).

The IR and NMR spectra were identical to those of N,N-1,5-dimethylpentamethylene-α-bromobenziminium tribromide prepared with cargbonyl bromide.

General procedure for the reaction of carbonyl bromide with ammonium halides. The ammonium halide (0·008 mol) was treated slowly with carbonyl bromide (0·25 mol) under N_2. Immediately the mixture turned deep red and a vigorous evolution of CO began. The mixture was stirred until no further gas evolved (*ca* 1 hr). The addition of dry ether (15 ml) and stirring caused the red viscous mixture to solidify. The orange to red colored tribromides were filtered and stored in a desiccator. These compounds were only slightly hygroscopic. However, they lost bromine on standing in air. The compounds prepared by this technique are described in Table 7.

Detection of carbon monoxide. The CO liberated by the reaction of carbonyl bromide with amides or ammonium halides was detected by the method of Kast and Selle.[39] As described above, the amide (or ammonium halide) was placed in a 50 ml 3-necked flask that was equipped with a septum, N_2 inlet and outlet. The outlet was connected to a trap at −100° that was, in turn, attached to a bubbler immersed in an ammoniacal $AgNO_3$ aq. This is darkened by CO, due to the precipitation of Ag.

A suitable soln was prepared by dissolving 1·7 g of $AgNO_3$ in water, to which was added 36 ml of 10% ammonium hydroxide and 200 ml of 8% NaOH aq and the volume made up to one liter with water. This soln was stored in a brown bottle in the dark.

After flushing with N_2 for 30 min carbonyl bromide was added by way of the septum and the gases liberated were

Table 7. Pertinent data of ammonium trihalides prepared using carbonyl bromide

Trihalide	Color	Yield, %	Mp°	lit. Mp°
Trimethylphenylammonium Tribromide	bright orange	96·2	115–116	112
N,N-Dimethylpiperidinium Tribromide[a]	red	100	69–72	
Tetramethylammonium Tribromide	orange	100	119·5–120·5	118[24a]
Pyridine Hydrobromide Perbromide	red	91·5	132–134	132–134[42]
Tetrapropylammonium Tribromide[b]	glistening orange	100	124–126	
Trimethylphenylammonium Dibromoiodide[c]	glistening orange	98	121–124	120[41]

[a]Anal. Calcd. for $C_7H_{16}Br_3N$: C, 23·88; H, 4·56. Found: C, 23·88; H, 4·54.
[b]Anal. Calcd. for $C_{12}H_{28}Br_3N$: C, 33·82; H, 6·62. Found: C, 33·81; H, 6·37.
[c]Recrystallized from nitromethane/ether.

carried with N_2 through the −100° trap (freezing out CO_2 and $COBr_2$) and bubbled into the $AgNO_3$ aq. An immediate darkening of the soln was observed indicating the liberation of CO. A reference ammoniacal Ag soln showed no darkening over a comparable amount of time.

General procedure for the reduction of α-bromobenziminium tribromides to the monobromides. Three different procedures for the reduction of tribromide salts (prepared from carbonyl bromide or PBr_5) to monobromides have been employed in this work. The methods are summarized below as A, B, and C, and are further illustrated specifically by the preparations that follow.

Method A. With this method the entire procedure was carried out in the anhyd atmosphere of the dry box. The tribromide was dissolved in the minimum amount of dry acetonitrile and a 2–3 molar excess of cyclohexene was introduced slowly. The originally red soln immediately became colorless and the addition of dry ether precipitated the white crystalline monobromide. Occasionally an oil was formed at this stage, however, it could easily be solidified by washing several times with dry ether. The monobromides were filtered and dried under vacuum (10^{-1} mm) for 12 hr. These salts can be stored for long periods of time in a desiccator (containing P_2O_5) that is kept in the dry box.

Method B. In order to eliminate the laborious isolation of the tribromides when the monobromides were actually desired, this method allows an *in situ* reduction of the tribromide. After the reaction of carbonyl bromide (or phosphorus pentabromide) with the amide was complete, 2–3 molar equivalents of cyclohexene were introduced into the mixture causing immediate discoloration. The addition of dry ether (or light petroleum 30–60°) then precipitated the monobromide. The supernatant was removed and the solid was washed several times with dry ether to remove impurities (PBr_3, $POBr_3$, 1,2-dibromocyclohexane). Until this point the procedure could be carried out in an anhyd atmosphere outside the dry box, making all additions and extractions by syringe through a septum. However, the isolation of the monobromide by filtration must be done in the dry box as was described under Method A.

Method C. This procedure allows the direct preparation of α-bromoiminium monobromides without having free bromine present in the mixture. This was accomplished by addition of cyclohexene to the solvent (or using cyclohexene as solvent) *before* the reaction of carbonyl bromide with the amide. The amide was dissolved in methylene chloride that contained 3–4 molar equivalents of cyclohexene and carbonyl bromide (3–4 molar equivs) was introduced slowly. As the tribromide is formed it is immediately reduced to the monobromide, which partially precipitates. Addition of dry ether completely precipitates the monobromide and it was collected in the dry box as previously described. This method is useful for the preparation of α-bromoiminium bromides which contain an aromatic nucleus that could be easily brominated, or other functionalities that are sensitive to free Br_2. It cannot, however, be used with PBr_5, since this reagent equilibrates with PBr_3 and free bromine. Carbonyl bromide does not react with cyclohexene.

These methods will be illustrated by one example each.

Reduction of N,N-*pentamethylene-α-bromobenziminium tribromide* (**7**) *to the monobromide* (**8**) *with cyclohexene* (*Method A*). Compound **7** (0·91 g, 0·0018 mol) was dissolved in 12 ml dry acetonitrile. The addition of cyclohexene (0·82 g, 0·01 mol) resulted in immediate discoloration and warming of the mixture. Dry ether (10 ml) was introduced and the white crystalline **8** (0·6 g, 100%) precipitated. The solid was filtered, washed with 20 ml dry ether, dried (2 hr at 20° and 10^{-1} mm/Hg) and stored in a desiccator in the dry box.

Analytical and physical data for N,N-pentamethylene-α-bromobenziminium bromide and other iminium bromides prepared using Method A are summarized in Table 1. IR and NMR data are given in Table 2.

Reaction of N-*methylbenzamide with phosphorus pentabromide and* in situ *reduction of the tribromide* (*Method B*). N-Methylbenzamide (4·1 g, 0·03 mol) was placed in a 50 ml 3-necked flask equipped with a septum and a N_2 inlet that was connected to a pressure release through a gas bubbler. Benzene (10 ml) was added and the system was flushed with N_2 for 30 min. PBr_3 (16·2 g, 0·06 mol) was introduced followed by the slow addition of Br_2 (9·6 g, 0·06 mol) while the flask was cooled with ice. The mixture was stirred for 30 min (2 hr for N,N-dialkylamides) and 8·2 g cyclohexene (0·1 mol) was added. The monobromide immediately precipitated, was washed with 20 ml benzene and transferred to the dry box. The solid was filtered, dried (1 hr at 20° and 10^{-1} mm/Hg) and sublimed (60°, 0·2 mm/Hg) to give 7·0 g (83·5%) of N-methyl-α-bromobenziminium hydrobromide, m.p. 133–136° dec (sealed tube).

The analytical and physical data for N-methyl-α-bromobenziminium hydrobromide and other monobromide salts prepared by Method B are summarized in Tables 1 and 3. IR and NMR data for these compounds are listed in Tables 2 and 4.

Reaction of N,N-*dimethylformamide with carbonyl bromide and simultaneous reduction of the tribromide* (*Method C*). N,N-Dimethylformamide (1·0 g, 0·014 mol) and 16·4 g (0·20 mol) of cyclohexene (used as solvent) were mixed in a 50 ml 3-necked flask equipped with a septum and a N_2 inlet system. After the system was

flushed with N_2 for 30 min 5·6 g (0·03 mol) carbonyl bromide was introduced slowly in two equal portions. A white solid immediately precipitated, 10 ml of dry ether was added and the reaction was continued for 0·5 hr. The supernatant was removed and the crystalline **45**,[26] m.p. 162–164° dec, was collected in the dry box (2·8 g, 95%) and purified by vacuum sublimation (65°; 10^{-2} mm/Hg).

IR and NMR data for iminium bromides prepared using Method A are summarized in Table 2. Analytical and physical data are in Table 1.

Reduction of N,N-1-*methylpentamethylene-α-bromobenziminium tribromides to the monobromide with mercury.* This procedure was carried out entirely in the anhydrous atmosphere of the dry box. N,N-1-Methylenepentamethylene-α-bromobenziminium tribromide (0·57 g, 0·0011 mol) was dissolved in the minimum amount of dry CH_2Cl_2 (8 ml). The addition of Hg (0·50 g, 0·0025 mol) caused the orange soln to become colorless with simultaneous precipitation of a solid. The solvent was decanted and dry nitromethane (15 ml) was added. The product dissolved and excess mercury and mercuric bromide were removed by filtration. Evaporation of nitromethane (40°, 25 mm/Hg) and treatment of the residue with CH_2Cl_2 (6 ml) gave 0·36 g (46·5%) of a non-hygroscopic white solid, m.p. 161–164°. Analytical and spectral data indicated that N,N-1-methylbenzamethylene-α-bromobenziminium monobromide was coordinated with a mercuric bromide molecule. Major spectral data are given in Table 2.

Conversion of N,N-*pentamethylene-α-bromobenziminium bromide* (**8**) *into the tribromide* (**9**). N,N-Pentamethylene-α-bromobenziminium bromide (0·60 g, 0·0018 mol) was placed in a 50 ml 3-necked flask equipped with a septum and the N_2 flush system previously described. Carbonyl bromide (0·95 g, 0·005 mol) was added through the septum and the resulting red mixture was stirred for 0·5 hr. The introduction of dry ether (10 ml) caused the quantitative precipitation (8·83 g) of the orange–red colored **7**, m.p. 94–96° (sealed tube).

The NMR and IR spectra were identical with those of an authentic sample.

8-*Tetrafluoroborate.* N,N-Pentamethylene-α-bromobenziminium bromide (13 g, 0·0039 mol) was suspended in 15 ml of dry ether. Triethyloxonium tetrafluoroborate (0·75 g, 0·0039 mol) dissolved in 10 ml CH_2Cl_2 was added and the mixture stirred for 15 min. Addition of 10 mol of dry ether precipitated 1·2 g (90·5%) crude product. Recrystallization from acetonitrile/ether gave 0·93 g (70%) N,N-pentamethylene-α-bromobenziminium tetrafluoroborate, m.p. 119–120° (sealed tube).

NMR (CD_3CN) δ 1·87 (m, 6, β and γ-H, pip. ring), 4·06 (t, 2, $J = 5$ Hz, α-CH_2, *cis* to phenyl), 4·45 (t, 2, $J = 5$ Hz, α-CH_2, *cis* to bromine), 7·70 (m, 5, C_6H_5), IR (mull) 3080 (w), 2948 (w), 2875 (w), 1622 (s, C=N$^+$), 1445 (s), 1285 (s), 1235 (s), 1185 (m), 1050 (broad vs, B—F), 870 (m), 850 (m), 755 (s), 695 (s), 660 (m) cm^{-1}. (Found: C, 42·21; H, 4·50. Calcd. for $C_{12}H_{15}BBrF_4N$; C, 42·39; H, 4·45%).

Reaction of N,N-*pentamethylene-α-bromobenziminium bromide* (**8**) *with aniline.* N,N-Pentamethylene-α-bromobenziminium bromide (1·33 g, 0·004 mol) was dissolved in dry acetonitrile (15 ml) and the system was kept under N_2 throughout the reaction. Aniline (0·93 g, 0·01 mol) was introduced and a white solid immediately precipitated. The mixture was stirred for 15 min and the ppt was filtered and washed with water (10 ml) to remove aniline hydrobromide. Recrystallization from chloroform/acetone gave 0·95 g (69%) of N,N-pentamethylene α-phenylbenzamidinium bromide, m.p. 261–263°.

NMR ($CDCl_3$) δ 1·77 (broad s, 6, β and γ-H pip. ring), 3·44 (m, 2, α-CH_2 *cis* to NHPh), 7·15 (m, 5, C_6H_5 C=N$^+$), 7·43 (s, 5, C_6H_5NH); IR (mull) 3050 (w), 2965 (w), 2850 (w), 1615 (s, C=N+), 1590 (s, aromatic C=C), 1440 (m), 1375 (m), 1252 (w), 765 (m), 715 (m), 700 (w), 690 (w) cm^{-1}; mass spec. *m/e* 265 parent peak. (Found: C, 62·83; H, 5·88; Br, 23·63. Calcd. for $C_{18}H_{21}BrN_2$: C, 62·61; H, 6·13; Br, 23·14%).

Labeling experiments with oxygen-18

(±) *Coniine.* 2-n-Propylpiperidine was prepared from conyrine, 2-n-propylpyridine (50·2 g, 0·416 mol) in glacial AcOH (125 ml) and in HCl aq (20 ml) over Adams platinum oxide (3·0 g) under shaking with H_2 in a Parr apparatus at 30–60 psi for 12 hr when the IR band at 1600 cm^{-1} completely disappeared. The base was isolated in the usual manner. (±) Coniine was resolved according to Craig and Pinder[40] with mandelic acid.

Benzoylconiine 0–18. Coniine (0·82 g; 0·00645 mol) and dry Et_3N (2·5 ml) were dissolved in dry $CHCl_3$ (5 ml). To this soln benzoyl chloride 0–18 (0·72 ml; 0·0050 mol) (60% atom enriched, IR 1780 (C=^{16}O), 1750 (C=^{18}O), 1720 cm^{-1}) in $CHCl_3$ (1 ml) was added with cooling and stirring. Et_3N HCl precipitated in 30 min. After 18 hr $CHCl_3$ (15 ml) was added and the whole washed with 10 ml portions water, 4 times with 2N H_2SO_4, again with water, once with 10% K_2CO_3 and dried ($MgSO_4$). Evaporation of $CHCl_3$ gave benzoyl coniine 0–18 (1·32 g; 88% yield), IR, 1630 cm^{-1} (C=^{16}O) and 1610 cm^{-1} (C=^{18}O); mass spectrum *m/e* 233 0–18 and 231 (M$^+$ 0–16).

Iminium salt (**6**) *and carbon dioxide oxygen*-18 *from benzoyl coniine* 0–18 *and carbonyl bromide.* Benzoyl coniine (**6** oxygen-18) (1 g; 0·0043 mol) from the above experiment in dry benzene (2·5 ml) in a 3-necked flask equipped with a dropping funnel and a N_2-inlet-outlet. The outlet was equipped with a gas collecting bottle. N_2 was bubbled through the soln and carbonyl bromide (0·65 ml; 2 equivs) in benzene (1 ml) was slowly added. This resulted, in a few minutes, in the precipitation of a red amorphous material. This was later identified as **6** (X = Br_3). The gas which formed was analyzed by the CEC-104 Mass Spectrometer of the Canadian Defense Research Board in Valcartier, Quebec. Results:

Peak	Compound	Height mm	%
44	$C^{16}O_2$	12	45
46	$C^{16}O^{18}O$	15	55

i.e. the CO_2 contained 45% and 55% $C^{16}O^{18}O$. Benzene was also present in the sample but its cracking pattern was not evident in the region of interest (40–48 *m/e*).

The iminium salt (**6**) was freed of unchanged benzoylconiine by decanting the benzene layer and triturating several times the amorphous material with benzene (yield, 1·69 g, 63%) evaporation of the benzene layer gave benzoyl coniine 0–18 (0·185 g, 18%). The amorphous salt gave IR 1600 cm^{-1} (C=N—); UV, λ max 235, 410 nm; NMR ($CDCl_3$), δ 1·0 (CH_3); 1·7–2·0 (m, CH_2); 4·3, 4·7 (m, H-2, H-6); 7·4 (s) and 7·9 (s), aromatic protons. Mass spec *m/e* 295, 297.

A part of the bromide was converted into the crystalline hexafluoroantimonate and another part decomposed by heating.

Hydrolysis of iminium salt **6** *with* $H_2^{18}O$. Iminium bromide **6** (0·68 g) was dissolved in dry acetonitrile (5 ml) to which was added from a syringe oxygen-18 labeled water (62·4 atom % 0–18; 13·7 atom % enriched D; Diaprep Inc.) followed by Et_3N (0·5 ml). After 1 hr the solvent was evaporated *in vacuo*, benzene added (10 ml), the soln filtered, and the Et_3N.HBr collected (0·51 g; m.p. 258–264°; literature m.p. 248–258°). This corresponded to 1·5 moles of HBr per mole of HBr per mole of iminium bromide. The above benzene soln was then completely evaporated to afford benzoyl coniine (0·37 g; 91% yield).

The IR spectrum showed peaks at 1630 cm^{-1} and 1610 cm^{-1} in the ratio of 3:2, identical with that in the labeled starting amide. TLC also showed complete identity.

Hexafluoroantimonate of **6**. Iminium bromide **6** (2·86 g; 0·0076 mol) was dissolved in dry nitromethane (5 ml) and slowly added from a dropping funnel to a soln of silver hexafluoroantimonate (3·611 g; 0·0075 mol) in dry nitromethane (5 ml). After 45 min the precipitated AgBr (1·26 g; 88%) was removed by filtration. The nitromethane soln was then evaporated to dryness under 0·1 mm pressure and the residue recrystallized from anhydrous chloroform/ether (1:1). This gave 1·03 g (25% based on the iminium salt) of a crystalline product m.p. 85–100°, with correct analytical figures (Table 1), incating a mixture of *cis-trans* isomers. By using Method B or C, for making the iminium monobromide, and converting it into the hexafluoroantimonate in methylene chloride as solvent an 85% yield of **6**-SbF_6, starting with optically active benzoyl coniine, was achieved.

Thermal decomposition of iminium bromide **5**. The non-crystalline iminium bromide (2·4 g) was dissolved in dry dibromoethane (20 ml) and refluxed for 3 hr. The dark colored soln was then washed with 9% $NaHCO_3$ aq, dried, and the solvent evaporated at 45°/20 mm Hg. The residue, containing a mixture of benzonitrile and 1,5-dibromooctane, was extracted with cyclohexane. Chromatography of 0·95 g oil on a silica gel column (20 g) with cyclohexane as eluent gave 1,5-dibromooctane (0·4 g; 20% yield). NMR (neat) δ 1·1 (*t*, 3·43) 1·7 (m, 10, CH_2); 3·4 (*t*, 2 CH_2); 4·1 (broad m, 1, CH). Mass spectrum 273, 271, 269 (M^+-1).

The yield of dibromooctane was considerably higher (up to 50%) when the tribromide of **6** was made, converted with cyclohexene, and the monobromide **6** thermally decomposed without a solvent on the vacuum line. No experiments were so far made with the separated geometrical isomers.

1,5-Dibromooctane was optically inactive when starting with optically active benzoyl coniine ($[\alpha]_D$ − 53°, neat) and following either technique.

Liberation of imidoyl bromides from their salts

N-*Methylbenzimidoyl bromide* (**14**) *from its hydrobromide*. N-Methylbenzimidoyl bromide hydrobromide (6·0 g, 0·022 mol) was suspended in 20 ml dry benzene contained in a 50 ml flask that was equipped with a reflux condenser. A glass tube N_2 inlet was positioned through the top of the reflux condenser to within 2 cm of the benzene level in the flask. The soln was refluxed and as the HBr was liberated it was removed from the system by the N_2 flow. It was found that this reaction was greatly facilitated by the rapid and efficient removal of HBr as it was liberated. After 3 hr the reaction was complete (as evidenced by the disappearance of the solid) and the benzene was evaporated. The residue was distilled (73–74°; 1 mm/Hg) to give 3·8 g (88·5%) of the extremely hygroscopic N-methylbenzimidoyl bromide (**14**).

The analytical and physical data for N-methylbenzimidoyl bromide and other imidoyl bromides prepared by a similar procedure are summarized in Table 3. IR and NMR data are given in Table 4.

Thermolysis of N,N-*pentamethylene-α-bromobenziminium bromide* (**8**) *without a solvent*. A 15 ml flask containing 1·8 g (0·0054 mol) on a vacuum line with a constant pressure of 10^{-3} mm/Hg. An adjacent trap cooled with liquid N_2 was used to collect the von Braun products (benzonitrile and 1,5-dibromopentane). The iminium bromide was heated at 150° for 13 hr, after which only 0·1 g (6%) of a black residue remained. The mixture of von Braun products (1·62 g, 92%) was collected in the trap. The IR and NMR spectra of the mixture proved to be identical to an authentic sample prepared by mixing molar amounts of benzonitrile and 1,5-dibromopentane.

Attempts to decompose N,N-pentamethylene-α-bromobenziminium bromide by heating in a solvent always led to lower yields of von Braun products. Separation by vapor phase chromatography is better than any technique of distillation or other purification methods.[41,43] Retention time for benzonitrile was 95·4 sec for 1,5-dibromopentane 275 sec. (Column was 6′ × 1/8″ stainless steel. G.E. (Silicone), 8% SF-96. Column temp 150°. Flow rate 18·2 ml/min).

Thermolysis of N,N-*pentamethylene-α-bromobenziminium bromide* (**8**) *in solution with isolation of* N-5-*bromopentylbenzimidoyl bromide* (**9**). To 0·8 g (0·0024 mol) of **8** in a 25 ml flask equipped with a reflux condenser was added 10 ml dry bromobenzene. A N_2 inlet connected to a pressure release through a bubbler was attached to the top of the reflux condenser. The mixture was heated at 100° for 24 hr, during which time it gradually turned dark. The thermolysis was followed by NMR, see Fig 1. The bromobenzene was removed at 35° (0·1 mm/Hg) leaving a dark residue. Extraction of this residue with 15 ml of dry chloroform and subsequent evaporation gave 0·55 g crude N-5-bromopentylbenzimidoyl bromide. A black ppt (0·25 g) which was insoluble in chloroform was not characterized. IR and NMR spectra indicated that the product was contaminated with benzonitrile and 1,5-dibromopentane. Further purification was not attempted since the imidoyl bromide decomposes upon distillation and is extremely hygroscopic. The NMR spectrum indicated that the crude product was 85% N-5-bromopentylbenzimidoyl bromide, therefore, giving an actual yield of 56%.

The temp used for this decomposition was very critical. Above 100° complete von Braun reaction occurred while below 100° the reaction rate was too slow to be useful. Even at 100° some von Braun products were formed.

Physical and spectral data for N-5-bromopentylbenzimidoyl bromide are summarized in Tables 3 and 4.

Hydrolysis. Bromide **9** (0·67 g, 0·02 mol) was stirred with 10 ml 2% NaOH for 30 min, extracted with chloroform (10 ml) to obtain 0·35 g (65%) of N-5-bromopentylbenzamide, m.p. 65–66°.

The IR and NMR spectra were identical to that of a sample of N-5-bromopentylbenzamide prepared by an independent synthesis.

Synthesis of N-5-*bromopentylbenzimidoyl bromide*

N-5-*Bromopentylphthalimide*. A mixture of potassium phthalimide (69 g, 0·372 mol) and 1,5-dibromopentane (258 g, 1·075 mol) was heated to 185° for 2 hr. Excess 1,5-

dibromopentane was removed at 100° (12 mm/Hg) and 75 ml of water was added. The resulting organic layer was taken up in 50 ml of chloroform, washed twice with 25 ml of water and dried with Na_2SO_4. Evaporation of solvent gave 94·5 g (83%) of crude product. Recrystallization from hot light petroleum (30–60°) yielded 83·5 g (79·5%) of N-5-*bromopentylphthalimide*, m.p. 60·5–61·5°. NMR (CCl_4) δ 1·75 (m, 6, $(CH_2)_3$, 3·36 (t, 2, $J = 6$ Hz, CH_2Br), 3·65 (t, 2, $J = 6$ Hz, $=N-CH_2$), 7·71 (s, 4, C_6H_4); IR (melt) 2950 (m), 2870 (w), 1770 (m), 1715 (vs, C=O), 1467 (m), 1435 (m), 1395 (s), 1370 (s), 1207 (w), 1188 (w), 1030 (m), 790 (w), 718 (s) cm^{-1}. (Found: C, 52·50; H, 4·78; Br, 27·08. Calcd. for $C_{13}H_{14}BrNO_2$: C, 52·70; H, 4·76; Br, 26·97%).

N-5-*Bromopentylamine hydrobromide*. To 83·5 g (0·36 mol) of N-5-bromopentylphthalimide was added 408 ml (3·63 mol HBr) of 48% HBr and 200 ml gl AcOH and the soln was refluxed (bath temp 125°) for 1 hr. The mixture was allowed to stand at room temp overnight, during which time phthalic acid crystallized. Phthalic acid was filtered off and the filtrate evaporated (50°, 25 mm/Hg) to dryness. The resulting solid was dissolved in 100 ml water and any remaining phthalic acid was filtered off. The water soln was evaporated to dryness and the residue recrystallized from EtOH to give 55·2 g (61·5%) of 5-bromopentylamine hydrobromide, m.p. 140–142° (*lit.*[42] m.p. 140–141°).

The NMR and IR spectra were consistent with the 5-bromopentylamine hydrobromide structure.

N-5-*Bromopentylbenzamide*. To 1·4 g (0·0057 mol) 5-bromopentylamine hydrobromide that was dissolved in 2 ml water was added 0·75 ml (0·69 g, 0·0064 mol) benzoyl chloride dissolved in 12 ml benzene. As the solution was stirred vigorously, 1·6 g (0·012 mol) K_2CO_3 dissolved in 10 ml water was introduced. The mixture was stirred for 2·5 hr at room temp after which no odor of benzoyl chloride was evident. The benzene layer was washed twice with 10 ml 10% K_2CO_3 aq then twice with 10 ml water. Drying with Na_2SO_4 and evaporation of benzene gave 1·53 g (100%) crude product. Recrystallization from acetone/water yielded 1·25 g (81·7%) N-5-bromopentylbenzamide, m.p. 65·5–66·5°. NMR ($CDCl_3$) δ 1·30–2·00 (m, 6, $(CH_2)_3$), 3·38 (t, 4, $J = 6$ Hz, $NHCH_2$ and CH_2Br), 6·70 (broad m, 1, CONH), 7·47 (m, 3, C_6H_5 *meta* and *para*-H), 7·80 (m, 2, C_6H_5 *ortho*-H); IR (melt) 3330 (s, N—H), 3070 (w), 2945 (s), 2870 (m), 1642 (vs, C=O), 1575 (m), 1525 (vs), 1488 (m), 1440 (m), 1305 (s), 800 (w), 708 (s), 690 (s) cm^{-1}. (Found: C, 53·08; H, 6·01; Br, 29·39. Calcd. for $C_{12}H_{16}BrNO$: C, 53·34; H, 5·97; Br, 29·58%).

Thermolysis of 5-bromopentylbenzimidoyl bromide (9). 5-Bromopentylbenzimidoyl bromide (0·5 ml) was heated neat at 125° in a sealed NMR tube for a total of 3 hr. The NMR spectrum before the heating was started showed a triplet at δ 3·34 for the bromomethylene group, a triplet at δ 3·63 for the methylene *alpha* to nitrogen and the aromatic multiplets at 7·44 (*meta* and *para* protons) and 8·01 (*ortho* protons). As the heating progressed, the aromatic resonance collapsed to a multiplet at δ 7·63, the triplet at 3·63 slowly disappeared and the triplet at 3·34 shifted to 3·45 and gradually increased in intensity to where it finally integrated for four protons. The final NMR spectrum, as well as the IR spectrum, was shown to be identical to an molar equiv mixture of benzonitrile and 1,5-dibromopentane. The product was also analyzed using a Carle gas chromatograph Model 6500 (Carbowax column 5′ × 1/8″, column temp *ca* 150°, He flow rate 20 ml/min) and shown to be composed of only benzonitrile (retention time 1·59 min) and 1,5-dibromopentane (retention time 3·95 min).

Degradation of 2,6-dimethyl-N-benzoylpiperidine without isolation of intermediates. 2,6-Dimethyl-N-benzoylpiperidine (6·5 g, 0·03 mol) was dissolved in 10 ml of dry CH_2Cl_2. The system was flushed with N_2 for 30 min before 16·3 g (0·06 mol) PBr_3 was introduced. Br_2 (9·6 g, 0·06 mol) was added slowly (system remained under N_2) and the mixture was stirred for 4·5 hr to insure complete reaction. The introduction of 7 ml (5·7 g, 0·07 mol) cyclohexene caused the originally red soln to become colorless as the Br_2 was absorbed. The addition of 20 ml of light petroleum (30–60°) resulted in the precipitation of the crude N,N-1,5-dimethylpentamethylene-α-bromobenziminium bromide. The supernatant was removed and the residue washed twice with 10 ml dry ether. The crude iminium bromide was distilled at 0·4 mm/Hg to give 8·2 g of a mixture of benzonitrile, 2,6-dibromoheptane and phosphoryl bromide, b.p. 60–85°.

The dibromide was purified according to the method of Johnson *et al.*[41] The distillate was poured into 10 ml of ice water to destroy phosphoryl bromide. The organic layer was taken up in 15 ml of light petroleum (30–60°) and benzonitrile was extracted 7 times with conc H_2SO_4 (3 ml for each 10 ml of the dibromide soln). The light soln was then washed twice with 10% NaOH (10 ml each time) and then 3 times with 10 ml portions water. The soln was dried over Na_2SO_4, evaporated, and the crude residue (4·8 g) distilled to give 4·4 g (58%) of 2,6-dibromoheptane, b.p. 121–123° at 25 mm/Hg (*Leonard and Nommensen*[18] *reported b.p.* 128–130° at 30 mm/Hg).

The product had NMR and IR spectra consistent with the dibromide structure.

Thermolysis of N,N-dimethyl-α-bromobenziminium bromide (16) *with isolation of N-methylbenzimidoyl bromide* (14). By a procedure similar to that previously described, N,N-dimethyl-α-bromobenziminium bromide (4·5 g, 0·0153 mol) was refluxed for 3 hr in 20 ml dry dibromomethane. Evidence of the thermal decomposition was given by the gradual disappearance of the solid iminium bromide. The solvent was removed at 30° (15 mm/Hg) and the residue was distilled at 0·05 mm/Hg to give 2·45 g (81%) N-methylbenzimidoyl bromide, b.p. 65–66°. If heating was continued for a longer period of time, the product was contaminated with benzonitrile, derived from complete von Braun degradation.

The physical and spectral properties of N-methylbenzimidoyl bromide have been listed in Tables 3 and 4.

Decomposition of N-methylbenzimidoyl bromide (14). N-Methylbenzimidoyl bromide (0·3 ml) was placed in an NMR tube and dissolved in 0·5 ml tetrachloroethylene. The tube was sealed and heated at 120° for 18 hr. The NMR spectrum before the heating started showed a singlet at δ 3·40 for the N-Me group and the aromatic multiplets at δ 7·30 (*meta* and *para* protons) and 7·96 (*ortho* protons). As the heating progressed, the aromatic absorptions collapsed to a multiplet at δ 7·44 and the singlet at δ 3·40 shifted to 2·53. It was demonstrated by comparison to authentic spectra that the multiplet at δ 7·44 was due to benzonitrile and the singlet at 2·53 corresponded to MeBr. No other peaks were present in the spectrum indicating a quantitative conversion. Also the IR spectrum of the residue, after tetrachloroethylene was removed (40°; 10 mm/Hg), showed the benzonitrile absorption at 2225 cm^{-1}.

N-Methylbenzimidoyl bromide was found to be thermally stable below 100°.

Thermolysis of N-ethylbenzimidoyl bromide. N-Ethylbenzimidoyl bromide (0·1 ml) was placed in an NMR tube and dissolved in 0·5 ml of tetrachloroethylene. The

tube was sealed and heated at 120° for 18 hr. The NMR spectrum before the heating began showed a triplet at δ 1·30 for the Me group, a quartet at 3·66 for the methylene hydrogens and the aromatic multiplets at 7·30 (*meta* and *para* protons) and 7·93 (*ortho* protons). Upon completion of the heating the aromatic signals had collapsed to a multiplet at δ 7·46, the triplet had shifted from 1·30 to 1·63 and the quartet from 3·66 to 3·32. It was shown by comparison to authentic spectra that the multiplet at δ 7·46 was due to benzonitrile and the triplet at 1·63 and quartet at 3·32 corresponded to EtBr. Evaporation of tetrachloroethylene (40°; 10^{-1} mm/Hg) gave a residue identified as benzonitrile by IR spectroscopy.

N-Ethylbenzimidoyl bromide was found to be thermally stable to 110°.

N-Methylbenzonitrilium fluorosulfate (**15**) *from benzonitrile.* Benzonitrile (6·8 g, 0·066 mol) and methyl fluorosulfate (7·6 g, 0·067 mol) were heated together under N_2 at 55° for 3 hr. The mixture slowly solidified and the ppt was washed with dry ether and filtered in the dry box to give 12·1 g (84%) of the crude product. Recrystallization from *o*-dichlorobenzene yielded 9·8 g (68%) pure N-methylbenzonitrilium fluorosulfate, m.p. 125–130° (sealed tube). NMR (CD_3CN) δ 4·06 (broad s, 3, CH_3), 7·87 (m, 5, C_6H_5); IR (mull) 3015 (w), 2375 (s, C=N-), 1725 (m), 1590 (m), 1265 (broad vs, SO_3), 1170 (m), 1055 (s), 932 (m), 750 (m), 695 (s) cm^{-1}.

N-Methylbenzonitrilium fluorosulfate was further characterized by hydrolysis to N-methylbenzamide in 92% yield.

N-Methylbenzonitrilium fluorosulfate (**15**) *from N-methylbenzimidoyl bromide* (**14**) *with methyl fluorosulfate.* This reaction was carried out entirely in the dry box. Methyl fluorosulfate (0·57 g, 0·005 mol) was added dropwise to 1·0 g (0·005 mol) N-methylbenzimidoyl bromide without the use of solvent. An immediate exothermic, vigorous evolution of MeBr resulted and the mixture solidified. The solid was washed with dry ether and filtered to give 1·1 g of crude product. The NMR spectrum indicated that the product was a mixture of N-methylbenzonitrilium fluorosulfate and N,N-dimethyl-α-bromobenziminium fluorosulfate in a ratio of 4:1. Based on this ratio, 1·1 g represents total yield of 94%. Recrystallization of the product mixture from *o*-dichlorobenzene gave N-methylbenzonitrilium fluorosulfate, m.p. 123–128° (sealed tube).

The NMR and IR spectra of the product were identical to an authentic sample. Further examples of the "Magic Methyl" reaction of imidoyl halides are given in Table 5 and Fig 5.

Addition of 20 mg LiBr in the NMR tube to the soln of N-ethylbenzonitrilium fluorosulfate results in the reappearance of the triplet of the benzimidoyl bromide at δ 3·61.

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