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Azidocarboxonium Ions[1)]

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The protonation of aroyl azides in superacidic media at low temperature (– 78 °C) occurs exclusively on the carbonyl oxygen leading to α-azidocarboxonium ions **2a – f**. The ^1H, ^{13}C, and ^{15}N NMR spectra of these ions indicate significant charge delocalization into the aryl ring as well as into the azido group. Upon warming up the solution these ions were, irreversibly, converted into benzoyl cations by loss of hydrozoic acid which was observed as protonated species.

Azidocarboxonium-Ionen[1)]

Aroylazide werden in supersaurem Medium bei tiefer Temperatur (– 78 °C) ausschließlich am Carbonylsauerstoffatom protoniert, was zu den α-Azidocarboxonium-Ionen **2a – f** führt. Die ^1H-, ^{13}C- und ^{15}N-NMR-Spektren dieser Ionen deuten auf eine merkliche Ladungsdelokalisation in den Arylring und die Azidogruppe hin. Beim Erwärmen der Lösungen wurden diese Ionen irreversibel in Benzoylkationen umgewandelt unter Abspaltung von Stickstoffwasserstoffsäure, welche in protonierter Form beobachtet wurde.

The protonation or complexation of the α-nitrogen as the first step in the Curtius rearrangement of aroyl azides catalyzed by a variety of Lewis and protic acids was suggested by *Newman* et al.[3)]. Subsequently *Fahr* et al.[4)] were able to isolate BF_3-complexes of aroyl azides at –60 °C. Their infrared investigation showed an unchanged azide absorption, whereas the frequency of the carbonyl absorption was lowered to 1645 – 1667 cm^{-1}. Based on this observation the authors suggested, that the Lewis acid attacks on oxygen. Similar results were obtained in the case of azidoformates[5)] and azidoformamidinium salts[6)].

Results and Discussion

We now wish to report the formation of α-azidocarboxonium ions by NMR spectroscopy *via* a direct protonation of acyl azides in superacidic media. The NMR data of the precursor azides **1a – f** and of the α-azidocarboxonium ions **2a – f** are summarized in Tables 1 and 2. The effectiveness of the mesomeric contribution of the aryl ring was examined by the comparison between chemical shift differences of the precursors and of the α-azidocarboxonium ions. Table 3 contains the differences ($\Delta\delta^{13}C$ and $\Delta\delta^{15}N$) of the ^{13}C and ^{15}N NMR chemical shifts. Analysis of the data obtained from ^{13}C study, presence of an OH resonance and the absence of $^{15}N-H$ coupling was an evidence for the formation of α-azidocarboxonium ions *via* the protonation of acyl azides. These ions have a remarkable stability and could be kept in SO_2 at –10 °C for several hours

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without any change in their NMR spectra. Removing the solvent led slowly to decomposition of these ions to the corresponding benzoyl cations by loss of hydrozoic acid as evidenced by ^{13}C and ^{1}H NMR spectra[7]. Moreover, the protonated hydrozoic acid was detected in the solution by ^{1}H and ^{15}N NMR spectroscopy.

The mesomeric structures **2A** – **D** of the α-azidocarboxonium ions indicate the positive charge delocalization into the aromatic ring and all three nitrogens.

Table 1. ^{13}C NMR Shifts[a] and ^{15}N NMR Shifts[b] of the Aroyl Azides **1** in ppm

Nr.	R	C_α	C-1	C-2,6	C-3,5	C-4	N-1	N-3
1a	H	172.37	130.55	128.55	129.25	134.22		
1b	CH_3	172.07	127.85	129.34	129.91	145.22		
1c	CH_3O	171.39	122.94	131.50	113.73	164.43		
1d	Br	171.69	129.44	130.80	131.99	129.68	125.34	239.25
1e	Cl	171.53	128.99[c]	128.99	130.74	140.93		
1f	F	171.14	126.80	132.00	115.75	166.51		
				(8.7)[d]	(22.0)[d]	(256.4)[d]		

[a] In $CDCl_3$ from internal TMS at 25 °C. – [b] In $CDCl_3$ from external, anhydrous ammonia at 25 °C. – [c] Confirmed by proton coupled spectrum. – [d] Coupling constants in Hz.

Table 2. ^{13}C NMR Shifts[a], ^{15}N NMR Shifts[b], and ^{1}H NMR Shifts[a] of the α-Azidocarboxonium Ions **2** in ppm

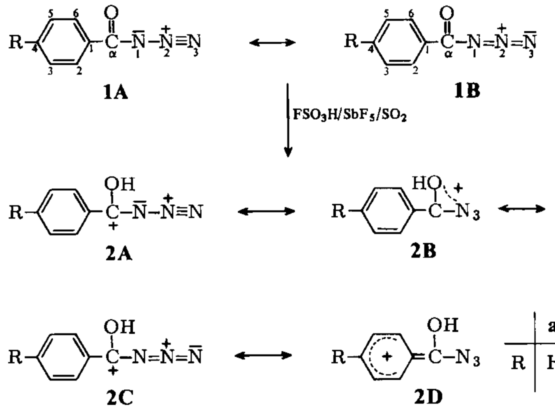
Nr.	R	C_α	C-1	C-2,6	C-3,5	C-4	N-1	N-3	OH
2a	H	184.71	121.46	131.53	130.17	141.43			11.8
2b	CH_3	183.59	118.50	131.85	131.34	156.23			11.7
2c	CH_3O[d]	180.88	113.42	135.53	116.48	170.26			12.3
2d	Br	184.45	120.57	134.49	133.01	139.48	153.67	261.64	12.3
2e	Cl	183.33	119.73	132.54	130.15	147.79			11.9
2f	F	182.52	117.27	135.06	117.84	170.17			11.8
				(12.0)[c]	(22.8)[c]	(268.1)[c]			

[a] In $FSO_3H/SbF_5/SO_2$ at – 80 °C from external TMS. – [b] In $FSO_3H/SbF_5/SO_2$ at – 80 °C referenced to external, anhydrous ammonia at 25 °C. – [c] Coupling constants. – [d] In FSO_3H/SO_2 at – 80 °C from external TMS[17].

Table 3. $\Delta\delta^{13}$C and $\Delta\delta^{15}$N Values of Ions **2** in ppm[a]

R	$\Delta\delta C_\alpha$	$\Delta\delta$C-1	$\Delta\delta$C-2,6	$\Delta\delta$C-3,5	$\Delta\delta$C-4	$\Delta\delta$N-1	$\Delta\delta$N-3
H	+12.34	–9.09	+2.98	+0.82	+7.21		
CH_3	+11.52	–9.35	+2.51	+1.43	+11.01		
CH_3O	+9.49	–9.52	+4.03	+2.75	+5.83		
Br	+12.76	–8.87	+3.69	+1.02	+9.80	+28.33	+22.39
Cl	+11.80	–9.26	+3.55	+0.59	+6.86		
F	+11.39	–9.53	+3.06	+2.09	+3.66		

[a] Positive values indicate deshielded shifts, negative values shielded shifts.



	a	b	c	d	e	f
R	H	CH_3	CH_3O	Br	Cl	F

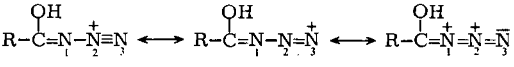
In order to study the charge distribution into the aromatic ring several *p*-substituted aroyl azides with electron withdrawing as well as electron releasing groups were prepared. We also prepared *p*-bromobenzoyl azide with ^{15}N label at N-1 and N-3 positions.

The chemical shifts for the *ortho* and *meta* carbons in the studied α-azidocarboxonium ions were assigned based on their observed chemical shift differences between the ions and their precursors (Table 3). The well-known studies on phenylcarbenium ions[8] and charge density calculations predict a higher difference in the chemical shifts for the *ortho* than *meta* carbons.

Data of Table 3 strongly indicate the mesomeric contribution of the ring carbons to the overall structure of the α-azidocarboxonium ions. The largest differences are observed for C-4 (*para* carbon), as expected. The downfield shift is the largest in **2b** ($\delta = 11$) and decreases in the *p*-halogenated systems **2d**–**f**. Furthermore, in **2c** the positive charge is substantially on the methoxy oxygen and this explains the small differences in $\Delta\delta$C-4. The same argument will be applicable in the case of **2f**, where because of the electron donating ability of flourine *via* resonance, $\Delta\delta$C-4 is the smallest in the series. The *ortho* and *meta* carbons are also deshielded and show a range of 2.5 – 4.0 ppm for C-2,6 (*ortho*) and 0.5 – 2.8 ppm for C-3,5 (*meta*). The substantial upfield shifts of C-1 (*ipso*) observed in a variety of cations generally confirm delocalization into the aryl ring[8]. Interestingly, little spread of the $\Delta\delta$C-1 values (0.5 ppm) were detected in the presently studied systems.

For the carbocationic center C_α we observed absorptions around $\delta^{13}C = 180$, about 9.5 – 12.8 ppm more deshielded relative to those of the neutral precursors.

The listed ^{13}C NMR data (Table 2) provide evidence for significant charge delocalization into the aryl ring. The best indicator for the extent of this mesomeric contribution is the observed C-4 shift. Comparing these shifts to those of other phenylcarboxonium ions show similarities with protonated benzoic acid and methyl benzoate[8,9]. In the latter two cases the charge is also significantly delocalized into the neighbouring heteroatom (i.e. oxygen). To determine the extent of positive charge delocalization into the neighbouring azide group in the observed azidocarboxonium ions, we prepared a ^{15}N enriched α-azidocarboxonium ion **2d**. The observed ^{15}N chemical shifts of the precursor (N-1 $\delta = 125.34$, N-3 239.25) are in good agreement to the known ^{15}N shifts of acyl azides[10]. In the corresponding α-azidocarboxonium ion **2d** we found absorptions for N-1 at $\delta = 153.67$ and for N-3 at 261.64, the differences in the shifts are 28.3 ppm (N-1) and 22.4 ppm (N-3), respectively, which is evidence for some positive charge on the azido function. Both results confirm the structural changes in the molecule and the charge distribution into the azido group involving mesomeric structure **3A**↔**3C**. However, structure **3C** with adjacent two positive charges gives very little stability.



$$\mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{1}{N}{-}\underset{2}{\overset{+}{N}}{\equiv}\underset{3}{N}} \longleftrightarrow \mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{1}{N}{-}\underset{2}{N}{=}\underset{3}{\overset{+}{N}}} \longleftrightarrow \mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{1}{\overset{+}{N}}{=}\underset{2}{\overset{+}{N}}{=}\underset{3}{\overset{-}{N}}}$$

3A **3B** **3C**

In recently reported aminodiazonium ions a similar range for N-3 ($\delta^{15}N\text{-}3 = 266-278$) was observed[11]. The lack of any proton coupling in the ^{15}N NMR spectrum of the presently studied ions clearly proves that the proton exclusively resides on the oxygen.

At −80 °C the exchange of the OH proton is still slow in magic acid and thus we were able to observe this proton in the ^{1}H NMR spectrum. The absorptions between $\delta = 11.8$ and 12.3 again are in good agreement to the shifts found in protonated esters[12] (about 12 ppm) with charge delocalization into the adjacent oxygen. The proton absorbs at $\delta = 14-16$ in protonated ketones[13], at about $\delta = 13$ in protonated carboxylic acids[14], and at about $\delta = 10$ in protonated amides[15]. The observed data further strengthen the argument that the heteroatom in α-position to the cationic center decreases the positive charge on the protonated oxygen.

In summary, ^{1}H, ^{13}C, and ^{15}N NMR studies at low temperature (−78 °C) prove the stabilization of the α-azidocarboxonium ions through the aryl ring and the azido group as well. The lack of any NH coupling particularly excludes the protonation on N-1 or N-3. Moreover, it has been shown that under the conditions of the present study the α-azidocarboxonium ions, on warming their solutions, do not give Curtius rearranged products. Instead, loss of hydrozoic acid leading to benzoyl cations was observed.

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Experimental Part

^{1}H NMR spectroscopy: Varian A56/60A NMR spectrometer, variable temperature probe, external TMS (capillary tube) as reference. – ^{13}C NMR spectroscopy: Precursors: Varian Model XL 200 spectrometer equipped with a broad-band probe, internal TMS as reference. Cations: Varian Model FT 80 spectrometer equipped with multinuclei broad-band variable temperature probe. External TMS (capillary tube) as reference. – ^{15}N NMR spectroscopy: Varian FT 80 spectrometer as described above. Reference anhydrous, external ammonia at 25 °C.

All aroyl azides were prepared by literature methods[16] and recrystallized from petroleum ether (40 – 60 °C) at about −25 °C. The ^{15}N-1 and ^{15}N-3 enriched aroyl azides **2d** were prepared with 30% enriched $Na^{15}NO_2$ using the same procedure. The terminal labeled compound was then stirred in DMF at 25 °C with a catalytic amount of NaN_3 for 4 h. Through precipitation with ice water and recrystallization from petroleum ether we obtained the ^{15}N-1 and ^{15}N-3 enriched compound. The intensity of the ^{15}N NMR signals showed a label distribution of 25% on N-1 and 75% on N-3.

Preparation of the α-azidocarboxonium ions **2**: A 1 : 1 mixture of freshly prepared FSO_3H and SbF_5 was diluted with SO_2 and cooled to −78 °C. The solid aroyl azides were slowly added at this temperature and the mixture was stirred until a homogeneous solution was obtained. The concentration of the solutions was 10 − 15%.

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[17] In this case, $FSO_3H/SbF_5/SO_2$ system, even at −80 °C, protonates the methoxy group and prevents its electron donating ability. The ^{13}C chemical shifts in this system are: δC_α = 183.86; C-1 118.75; C-2,6 135.34; C-3,5 123.02; C-4 158.17; OCH_3 72.19.

[88/83]