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A Fourier Transform Ion Cyclotron Resonance Study of the Structure of Some Phenyl-substituted 2-Azaallenium Ions

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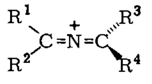
It is shown by proton abstraction reactions in combination with deuterium labelling that the initial structure of the ions **1** – **3** generated by electron impact from some benzylideneamines through loss of an alkyl radical via α-cleavage is indeed that of phenyl-substituted 2-azaallenium ions. The deprotonated species appear to have very high gas-phase basicities, that are higher than 231.7 kcal/mol.

Eine Fourier-Transform-Ionen-Cyclotron-Resonanz-Studie zur Struktur von Phenyl-substituierten 2-Azaallenium-Ionen

Durch Protonenabstraktionsreaktionen in Kombination mit Deuterium-Markierungsexperimenten wird gezeigt, daß die Ionen **1** – **3**, die durch Elektronenstoß aus Benzylidenaminen durch Alkylradikal-Abspaltung aus der α-Position erzeugt werden, die Struktur von Phenyl-substituierten 2-Azaallenium-Ionen besitzen. Die durch die Deprotonierung entstehenden Moleküle zeigen sehr hohe Gasphasenbasizitäten (größer als 231.7 kcal/mol).

In previous papers[1a, b)] the gas phase chemistry of some metastable phenyl-substituted 2-azaallenium ions **1** – **3** has been described. Ion **1** eliminates H$^\bullet$ and HCN, **2** loses H$^\bullet$, HCN, and C_6H_6, and **3** expels preferentially H$^\bullet$ and C_6H_5CN (>97%) but HCN to a very minor extent only (<0.5%).



	R^1	R^2	R^3	R^4
1	C_6H_5	H	H	H
2	C_6H_5	H	C_6H_5	H
3	C_6H_5	C_6H_5	H	H

D- and ^{13}C-labelling have shown that the neutral HCN lost from ion **1** exclusively contains the benzylidene hydrogen and carbon atom. The same is true for ion **2** where exclusively the benzylidene hydrogen atoms are retained in the eliminated HCN as proved by D-labelling. These observations together with the exclusive loss of C_6H_5CN from ion **3** have ruled out any possible phenyl group or hydrogen atom migration in

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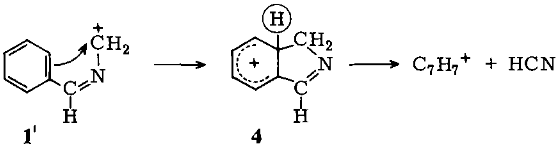
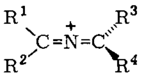
these eliminations. They proceed via an intramolecular electrophilic substitution reaction at the *ortho* position of the phenyl ring (shown for ion **1** in eq. 1), which, according to MNDO calculations, is energetically more favoured than all alternative pathways inspected, i.e. a 1,2-phenyl or a 1,2-H shift, or an *ipso* substitution reaction in the ions **1**[1b)].



1' **4**

(1)

In this paper we have addressed ourselves to the question whether proton/deuteron abstractions from the ions **1a – c**, **2a**, **b**, and **3a** with suitable bases could give information about their structures (for example **1** and/or **4**) thereby simultaneously yielding an estimate of their gas-phase acidities. To this end we have used the method of Fourier transform ion cyclotron resonance[2,3] which offers the possibility to eject ions[4,5] selectively from the cell, so that interfering reactions of such ions can not occur anymore. All ions **1a – c**, **2a**, **b**, and **3a** have been generated from the corresponding benzylideneamines by electron impact induced loss of an alkyl radical *via* the well-known α-cleavage as described before[1)].



	R^1	R^2	R^3	R^4
1a	C_6H_5	D	H	H
1b	C_6H_5	H	D	D
1c	C_6H_5	H	H	H
2a	C_6H_5	D	C_6H_5	D
2b	C_6H_5	H	C_6H_5	D
3a	C_6H_5	C_6H_5	H	H

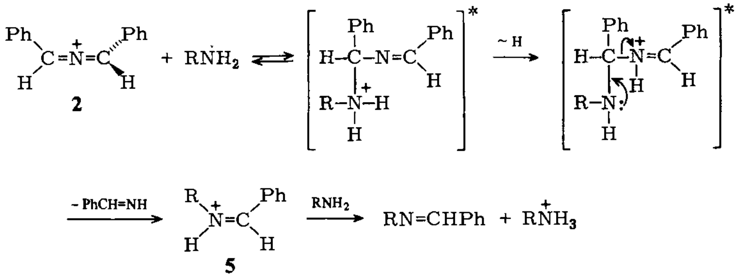
Results and Discussion

Several amines of high basicity[6)], such as $(CH_3)_2N[CH_2]_nNH_2$ (n = 2, 3) and $H_2N[CH_2]_nNH_2$ (n = 3, 5) have been allowed to react with the ions **1** and **2** in separate experiments.

After ejection of all ions, with the exception of **1** or **2**, protonated amines are formed in high abundance and ejection of **1** or **2** shows that they are their precursors. However, closer examination shows that this is not due to proton abstraction from the ions **1** or **2**, but to a side-reaction shown for **2** in Scheme 1.

It can be seen from Scheme 1 that ejection of **2** will influence the abundance of the protonated amines, but not because of a direct proton transfer reaction: ion **5** is the actual proton donor (in the reaction of ion **1** both expected product ions **5** and $R\overset{+}{N}H = CH_2$ are formed in a ratio of ≈1:9). In reactions with α,ω-bis(dimethylamino)alkanes ($(CH_3)_2N[CH_2]_nN(CH_3)_2$) this channel is absent and ion **5** is not formed, because the 1,3-H-shift is not possible anymore. Nevertheless, even with 1,4-bis(dimethylamino)butane (**6**), which has the highest gas-phase basicity known[6)], it has not been possible to abstract a proton from either of the ions **1**, **2**, and **3**.

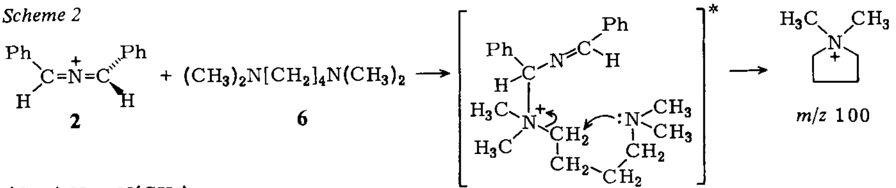
Scheme 1

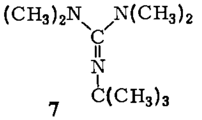


$R \triangleq (CH_3)_2N[CH_2]_2-,\ H_2N[CH_2]_3-,\ (CH_3)_2N[CH_2]_3-,\ H_2N[CH_2]_5-$

Instead of proton abstraction a slow formation of ions *m/z* 100 is observed in the reactions of **6** with the ions **1** and **2**; this is probably due to formal transfer of a $(CH_3)_2N^-$ group from **6** to these ions as shown for **2** in Scheme 2.

Scheme 2





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However, compound **7**, the synthesis and properties of which have been discussed by *Barton*[7], readily abstracts a proton from the ions **1**, **2**, and **3**. Unfortunately, it has not been possible to measure the gas-phase basicity of **7**, because no base, not even **6**, is able to abstract a proton from the conjugate acid of **7**; this result precludes both equilibrium measurements[6] and bracketing studies[8].

The latter, not the former, could have been applied to the present ions **1**, **2**, and **3** to obtain an estimate of their gas-phase acidities (or basicities of the corresponding deprotonated species) because these are fragment ions, whereas their deprotonated forms are chemically too unstable species to introduce them into the mass spectrometer.

The only statement, which can be made in this respect, is that the gas-phase basicities of the deprotonated species of **1**, **2**, and **3** are higher than that of **6** (being 231.7 kcal/mol[6]), but lower than that of **7** which obviously is not only a very strong base in solution[7], but also in the gas-phase. The percentages of proton and deuteron abstractions from ions **1a – c**, **2a, b**, and **3a**, which take place in the reaction with base **7**, have been compiled in Table 1.

This Table shows that neither of the ions **1**, **2**, and **3** transfers an aromatic ring proton to base **7**, thus excluding a structure such as **4** as an alternative for **1** (see eq. 1) which would be expected to transfer the encircled proton. Also another structure such as **8** is not very likely, because this would have a much higher acidity than observed[9].

$C_6H_5{-}CH_2{-}\overset{+}{N}{\equiv}C{-}H$

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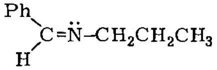

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It may be concluded, therefore, that the ions **1**, **2**, and **3** have the structures as at their formation.

Table 1. Percentages of Proton and Deuteron Abstraction from Ions **1a – c**, **2a, b**, and **3a** by base **7**

Ion	H^+ abstraction	D^+ abstraction
1a	82	18
1b	51	49
1c	100	–
2a	–	100
2b	60	40
3a	100	–

Note the isotope effect of 1.5 in the proton versus deuteron abstraction from ion **2b** (Table 1). An isotope effect will also be operative in the proton versus deuteron abstraction from the ions **1a** and **1b**, but in these cases the non-aromatic hydrogen/deuterium atoms do not possess equivalent positions such as in ion **2b**. Suppose that in addition to an isotope effect i, which favours the abstraction of a proton over that of a deuteron, a preference p exists for abstraction of a proton from the terminal methylene group over abstraction of a proton from the benzylidene position of ion **1**. Then the equations

$$2p\,i = \frac{82}{18} \text{ for } \mathbf{1a} \text{ and } \frac{i}{2p} = \frac{51}{49} \text{ for } \mathbf{1b}$$

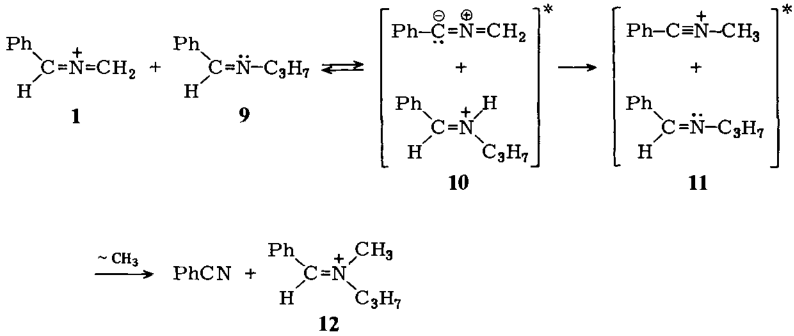
hold, from which i and p can be calculated to be 2.2 and 1.0, respectively. Thus, there is no preference for abstraction of a proton from either the benzylidene or the methylene position of ion **1** by base **7**.

Finally, it should be mentioned that the ions **1** do not transfer a methyl cation either to base **7** or to base **6** in agreement with their structure, but interestingly they do in reaction with their neutral precursor **9**.

Reactions of the labelled ions **1a – c** show that the transferred methyl cation contains hydrogen from the benzylidene and methylene groups, but not any of the phenyl ring hydrogen atoms. The methyl cation transfer probably proceeds as given in Scheme 3.

The initial proton transfer step, leading to the encounter complex **10**, is endothermic and therefore this complex cannot dissociate. Reprotonation can either occur on the ylide carbon position leading back to the initial reactants, or on the methylene position leading to complex **11** in which a facile methyl cation transfer can now take place to give ion **12**. Apparently, the collision partner assists in transferring a proton from the benzylidene to the methylene position, as long as no exothermic pathway, such as proton transfer or a reaction similar to that shown in Scheme 1 or Scheme 2, is available. As such this process bears some resemblance with hydrogen/deuterium

Scheme 3



exchange, which is observed both in cationic[10,11] as well as in anionic[12,13] gas-phase chemistry.

MNDO Calculations on the Gas-Phase Acidity of 2-Azaallenium Ions

In addition to the experimental ICR-work molecular orbital (MO) calculations were performed in order to gain information about the gas-phase acidity[14] of the 2-azaallenium ions **1**, **2**, and the parent system **13** $CH_2=\overset{+}{N}=CH_2$. The size of the cations **1** and **2** precludes the application of higher basis set *ab initio* calculations; however MNDO calculations[15] have proved to give gas-phase acidity data which are in good agreement with experimental and *ab initio* data[16].

The experimental results (vide supra) have shown that the superbase **7** abstracts a proton from the methylene positions of the ions **1** – **3**, but not from the phenyl ring positions. Therefore we conclude that a neutral species of the nitrile ylide type[17] is the most likely candidate as the primary deprotonation product. Nitrile ylides are highly reactive 1,3-dipoles whose cycloaddition chemistry is of great theoretical and experimental interest.

Structures and energies[18] of the nitrile ylides **14** – **17** were evaluated using complete optimization MNDO calculations. Together with the calculated data for the cations **1**, **2**, and the parent system **13** it is possible to determine theoretical gas-phase acidity data from the equation given in Table 2.

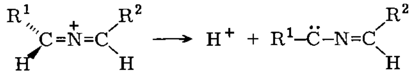
A gas-phase acidity of 237.9 kcal/mol is calculated for the parent system **13**, the 2-azaallenium ion $CH_2=\overset{+}{N}=CH_2$. This figure indicates that 2-azaallenium ions are very weak cation-acids, compared to other positively charged systems[6,14]. On the other hand the corresponding nitrile ylides appear to be extremely strong neutral bases. In the reverse reaction of their formation, protonation of nitrile ylides is expected to take place at the carbon atom[19] in contrast to most other strong neutral bases of the amine type, which are protoned at the nitrogen atom[6].

Introduction of a phenyl substituent into the 2-azaallenium system *lowers* the gas-phase acidity further (MNDO gives 240.4 kcal/mol for **1**), mainly due to the increased stabilization of the cation; the stabilization of the nitrile ylide **15** is expected to be less significant. Ion **1** loses protons mainly from the benzylidene position thus giving nitrile ylide **15**; loss of a proton from the 3-position is 4.4 kcal/mol more endothermic thereby leading to nitrile ylide **16** (R^1 = H; R^2 = Ph).

A second phenyl substituent in 3-position as in ion **2** lowers the gas-phase acidity again (244.4 kcal/mol). Favourable interactions between phenyl-substituents and the C – N – C unit lead to high thermodynamic and kinetic stability for both the cation **2**[20] and the nitrile ylide **17**.

The calculated gas-phase acidities in the range of 237 – 245 kcal/mol explain the experimental failure to abstract protons from gaseous 2-azaallenium ions using conventional nitrogen bases of the amine type. The primary products, the nitrile ylides **14** – **17** themselves, are the strongest neutral bases known; only superbase **7** seems to be competitive, but experimental data for its gas-phase acidity are not yet available.

Table 2. Calculated MNDO Heats of Formation (ΔH_f^0) and Gas-Phase Acidities (ΔH_r^0) (kcal/mol)[a]



1, 2, 13 **14 - 17**

	R^1	R^2	ΔH_f^0	R^1	R^2	ΔH_f^0	ΔH_r^0
13	H	H	212.3 → **14**	H	H	83.2	237.9
1	Ph	H	223.3 → **15**	Ph	H	96.7	240.4
			↘ **16**	H	Ph	101.1	244.8
2	Ph	Ph	238.1 → **17**	Ph	Ph	115.5	244.4

[a] ΔH_f^0 (H^+) = 367.0 kcal/mol.

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Experimental Part

The experiments have been performed using a home-made FT-ICR spectrometer. Details concerning the essential hardware[21], software[22], and general operating procedures[5,23,24] have been described elsewhere.

The compounds were introduced *via* "leak valves" to pressures of ≈25 µPa and ionized by electron impact at energies of 12 – 15 eV. The ions were trapped in a cubic inch cell by a magnetic field of 1.4 T and a trapping voltage of ≈1 V. The ions of interest were selected by ejection of all other ions. This was achieved by a pulse (of sufficient amplitude to eject all ions) which, at the resonance frequency of the ion of interest, was phase shifted by 180°. This created a notch in the waveform of this pulse[25]. In practice[26], this was done by applying two consecutive pulses of the same amplitude (typically 3.5 V peak to peak) and scan-rate (typically 25 kHz/ms). The initial frequency of the frequence sweep of the second pulse was chosen to be equal to the final frequency of the first pulse, which frequency was made equal to the resonance frequency of the ion of interest. The second pulse started with the phase shifted 180° with respect to the first pulse. This resulted in ejection of all ions except the one with resonance frequency at the notch. In this way, the chemistry of this single ion could be investigated.

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[1] [1a] For an early study see *S. Hammerum*, J. Chem. Soc., Perkin Trans. 2 **1973**, 854; Review: *H. Schwarz* and *C. Köppel*, in *S. Patai*, The Chemistry of Ketenes, Allenes and Related Compounds, p. 189, Wiley Interscience, New York 1980. – [1b] *E.-U. Würthwein, H. Halim, H. Schwarz*, and *N. M. M. Nibbering*, Chem. Ber. **115**, 2626 (1982).

[2] *M. B. Comisarow*, in *P. R. Griffiths*, Transform Techniques in Chemistry, chapter 10, Plenum Press, New York 1978.

[3] *C. L. Wilkins* and *M. L. Gross*, Anal. Chem. **53**, 1661 (1981).

[4] *M. B. Comisarow, V. Grassi*, and *G. Parisod*, Chem. Phys. Lett. **57**, 413 (1978).

[5] *J. C. Kleingeld* and *N. M. M. Nibbering*, Org. Mass Spectrom. **17**, 136 (1982).

[6] *D. H. Aue* and *M. T. Bowers*, in *M. T. Bowers*, Gas Phase Ion Chemistry, Vol. 2, chapter 9, Academic Press, New York 1979.

[7] *D. H. R. Barton*, presented at the Organic Synthesis Meeting, Oxford, G.B., June 1981. – *D. H. R. Barton, J. D. Elliot*, and *S. D. Gero*, Chem. Commun. **1981**, 1136, J. Chem. Soc., Perkin Trans. 1 **1982**, 2085.

[8] *M. S. B. Munson*, J. Am. Chem. Soc. **87**, 2332 (1965).

[9] For example, the basicity of methyl isocyanide is ≈ 10 kcal/mol higher than that of acetonitrile as derived from *A. J. Illies, S. Lin*, and *M. T. Bowers*, J. Am. Chem. Soc. **103**, 5674 (1981). Using this information the acidity of ion **8** can be estimated to lie in the range of 190 – 210 kcal/mol.

[10] *B. S. Freiser, R. L. Woodin*, and *J. L. Beauchamp*, J. Am. Chem. Soc. **97**, 6893 (1975).

[11] *D. P. Martinsen* and *S. E. Buttrill jr.*, Org. Mass Spectrom. **11**, 762 (1976).

[12] *C. H. DePuy* and *V. M. Bierbaum*, Acc. Chem. Res. **14**, 146 (1981).

[13] *S. Ingemann, J. C. Kleingeld*, and *N. M. M. Nibbering*, presented at the NATO Advanced Study Institute on Chemistry of Ions in the Gas Phase, Vimeiro, Portugal, 6. – 17. September 1982. The proceedings of this conference will be published as a volume in the NATO ASI series.

[14] *R. A. Eades, D. A. Weil, D. A. Dixon*, and *C. H. Douglas jr.*, J. Chem. Phys. **85**, 981 (1981), and references therein. Quantum mechanical calculations give ΔH-values, whereas our experimental ICR-data are ΔG-values.

[15] *M. J. S. Dewar* and *W. Thiel*, J. Am. Chem. Soc. **99**, 4899, 4907 (1977).

[16] *J. Chandrasekhar, J. G. Andrade*, and *P. v. R. Schleyer*, J. Am. Chem. Soc. **103**, 5609, 5612 (1981).

[17] [17a] *R. Huisgen, H. Stangl, H. J. Sturm, R. Raab*, and *K. Bunge*, Chem. Ber. **105**, 1258 (1972). – [17b] *K. Bunge, R. Huisgen, R. Raab*, and *H. Stangl*, Chem. Ber. **105**, 1279 (1972). – [17c] *K. Bunge, R. Huisgen, R. Raab*, and *H. J. Sturm*, Chem. Ber. **105**, 1307 (1972). – [17d] *K. N. Houk*, Top. Curr. Chem. **79**, 1 (1979).

[18] Detailed information concerning the MNDO results are available from *E.-U. Würthwein*, upon request.

[19] *K. Bunge, R. Huisgen*, and *R. Raab*, Chem. Ber. **105**, 1296 (1972).

[20] *E.-U. Würthwein*, Angew. Chem. **93**, 110 (1981); Angew. Chem., Int. Ed. Engl. **20**, 99 (1981).

[21] *J. H. J. Dawson*, in *H. Hartmann* and *K.-P. Wanczek*, Lecture Notes in Chemistry, Vol. 31, p. 331, Springer-Verlag, Berlin 1982.

[22] *A. J. Noest* and *C. W. F. Kort*, Comput. Chem. **6**, 111 and 115 (1982).

[23] *J. C. Kleingeld* and *N. M. M. Nibbering*, in lit.[21], p. 209.

[24] *S. Ingemann, N. M. M. Nibbering, S. A. Sullivan*, and *C. H. DePuy*, J. Am. Chem. Soc. **104**, 6520 (1982).

[25] *A. J. Noest* and *C. W. F. Kort*, Comput. Chem., in press.

[26] *J. C. Kleingeld* and *N. M. M. Nibbering*, Tetrahedron, in press.

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