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A NEW ROUTE TO METHYLENIMINE VIA PYROLYSIS OF AZETIDINE

V.V.Volkova, L.E.Gusel'nikov*, V.N.Perchenko, V.G.Zaikin,
E.I.Eremina, N.S.Nametkin
Topchiev Institute of Petrochemical Synthesis, USSR Academy of Sciences,
Moscow 117071, USSR

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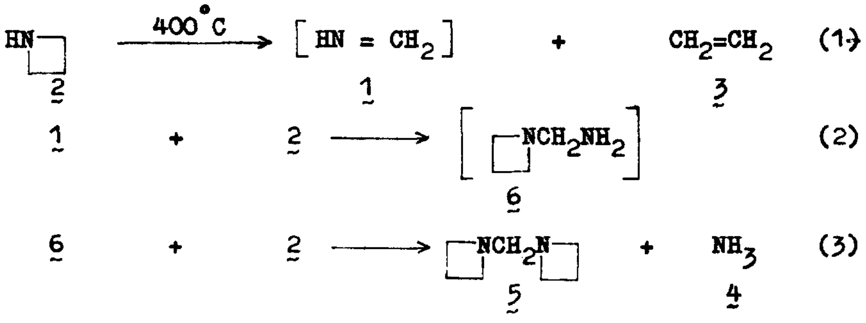
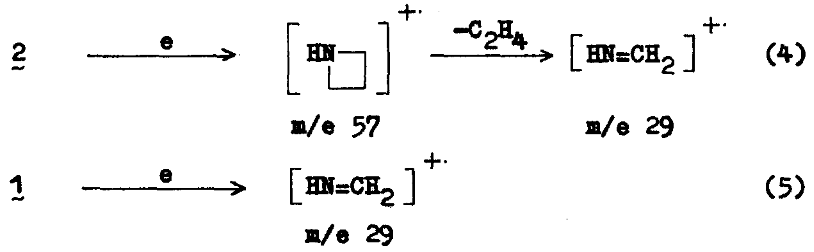
Unstable intermediates containing a $(p - p)_\pi$ bond between carbon and another element, for example, silicon-carbon[1], germanium-carbon[2,3], phosphorus-carbon[4], sulfur-carbon[5] are of considerable theoretical interest. One of these, methylenimine (1) is the prototype of nitrogen-carbon double bonded compounds. Together with formaldehyde and thioformaldehyde this compound has been detected in interstellar space[6]. It was also observed in a gas phase under low pressure (microwave[7,8], photoelectron[9] and mass spectrometry[10]) and in the rare gas matrices at 4 K (ir spectroscopy) using pyrolysis[13-15] and photolysis[11-16] of methylazide, pyrolysis of methylamine[6,8] and matrix photolysis of diazomethane[12] for its generation.

In our recent work[17] on gas phase pyrolysis of azetidine (2) we have found that ethylene (3), ammonia (4) and bis(azetidino)methane (5) were the main reaction products. The following reaction scheme involving transient 1 has been suggested:



We now report evidence for this mechanism based on spectral data of 1 and trapping experiments. Low pressure pyrolysis of 2 ($3\cdot10^{-3}$ torr, 400-700°C) in a flow system was used to detect 1 in a gas phase (by mass spectrometry) and in a solid state (by low temperature ir spectroscopy). To observe 1 in a gas phase a furnace was placed on a quartz tube close to the ionization chamber of the mass spectrometer. An increase in intensity of the m/e 29 ion peak (relatively to the parent ion peak m/e 57) was observed above 500°C[18]: Two paths for the formation of the m/e 29 ion should be considered: (i) the fragmentation of the molecular ion m/e 57 (reaction 4)[19,20] and (ii) the ionization of the neutral molecule 1 (reaction 5):



The reaction 4 is not likely to be responsible for the increase of the I_{29}/I_{57} ratio. Therefore the increase of this ratio as high as 2,5 times at decomposition temperatures should be interpreted in terms of the reaction 5[21].

Low temperature ir spectra of the pyrolysis products of 2 were obtained on an Unicam SP 1200 spectrometer equiped with an optical cryostat R46 FTINT containing a quartz tube heated to 500–800°. The products were frozen out onto a potassium bromide window target cooled with liquid nitrogen, located about 6 cm from the exit end of the furnace. Several new absorption bands were observed in the spectrum as 2 was being decomposed. These are 945, 955, 1440, 1444, 2975, 3065, 3090 cm^{-1} absorptions due to 3[22] and ones at 1070, 1121, 1182, 1418, 1459, 1640, 2893, 2921, 2993, 3160, 3260 cm^{-1}. All absorptions disappear as the sample temperature increases but unlike the former set of absorptions the second one can not be reproduced when the pyrolysis products were evaporated and re-condensed on the target.

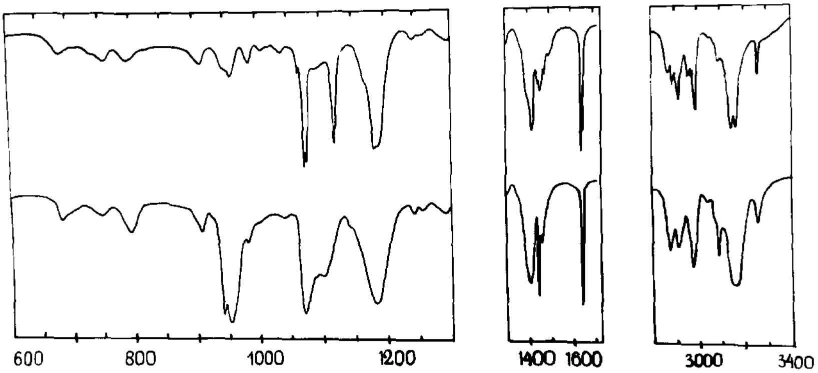
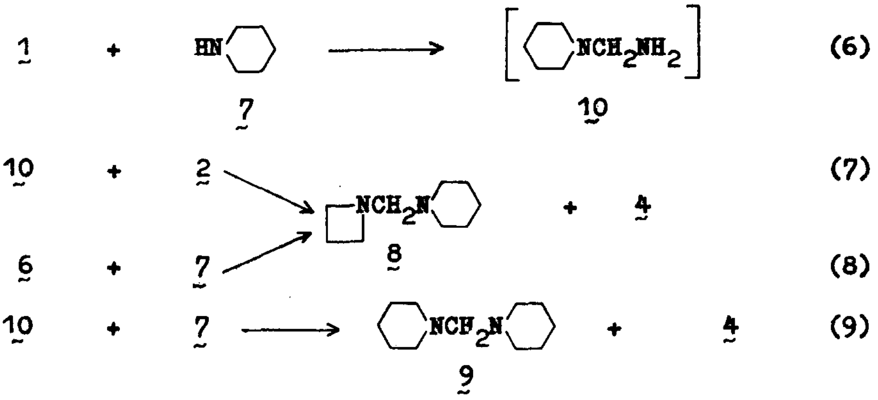


Figure. Low temperature spectra of the pyrolysis products of 2

The lower spectrum of the 750°C pyrolysis products of 2 shown in the figure reveals mainly the above mentioned absorptions. Only the weak bands of starting material are observed. The upper spectrum represents the same sample remedied by controlled annealing with warming up to 146 K followed by freezing down to 77 K. As a result 3 leaves the target and remaining sample is crystalized (see splitting of the bands). The split bands belong to the one reaction product since their intensities change together with the target temperature[23]. A certain coincidence of some absorptions observed in this work with those[11] calculated for 1 has been found. No absorptions due to 4 and 5 were detected when increasing the target temperature. These compounds were identified in an ir spectrum only when the evaporation and re-condensation of the sample on the target was carried out. Therefore reaction 3 occurs in a gas phase but not on the target[24].

A stabilization of 1 at 77 - 153 K found in this work is advantageous for the investigation of the chemical properties of unstable 1. Thus we have found that the vapor-deposition of piperidine (7) on frozen 1 followed by warming results in (piperidinoazetidino)methane (8) and bis(piperidino)methane (9) as well as 4:



Corresponding methylendiamines were formed when condensing other cyclic imines on frozen 1. They can be also produced by co-pyrolysis of 2 and cyclic imines in a flow reactor under inert atmosphere. For instance, the co-pyrolysis of 2 and 7 (molar ratio 2:1) yields 4 (29,7%), 8 (48,6%) and 9 (14,4%). The higher is the concentration of 7 in an initial mixture, the greater is the amount of last two products.

Further work is continuing in this area.

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19. The intensity of the m/e 28 peak ($M^{+\cdot}$ ion of 3) increases similarly.
20. At 19 ev the abundance of the fragment ion constitutes 27% of the m/e 57 peak.
21. This ratio for the fragment ion m/e 29 remains constant.
22. Absorptions of 3 in an argon matrix are observed at 946,5, 1439,5, 2994 and 3111 cm^{-1}; see A.E.Barnes, J.D.R.Howells, J.Chem.Soc.Faraday II, 69, 532 (1973).
23. The intensities of the cited bands remain unchanged up to 153 K and disappear completely at 188 K.
24. Disappearance of 1 on a target with the temperature is responsible for the observation of a number of bands (754, 1008, 1295, 1130, 1725 and broad 3100-3300 cm^{-1}) which are possibly due to 6.