Tetrahedron Letters No. 35, pp 3067 - 3070, 1977. Pergamon Press. Printed in Great Britain.

EXPLORATORY COLD PLASMOCHEMISTRY IN ORGANIC SYNTHESIS
I - PLASMOLYSIS OF SOME LINEAR AND CYCLIC SECONDARY AMINES

B. FIXARI and P. CAUBERE*

Laboratoire de Chimie Organique I, ERA CNRS n° 476, Université de Nancy I
Case Officielle 140, 54037 Nancy Cédex (France)

M. FELDEN

Laboratoire de Physique des Milieux Ionisés, Université de Nancy I
Case Officielle 140, 54037 Nancy Cédex (France)

(Received in UK 10 June 1977; accepted for publication 5 July 1977)

Introduction

Cold plasmas[1] are fascinating potential synthetic tools for Organic Chemistry. As a matter of fact, it is known from the few examples described in the literature, that the first step of a plasma process is the formation of highly energetic species at near ambiant temperature. The evolution of these intermediates, obviously, depends upon the post-discharge conditions as well as the conditions in the discharge itself. It may be expected that Organic Plasmochemistry will lead to new and unusual synthesis if the conditions are well selected. Moreover, plasmolysis of organic substrates will be a good synthetic method, even with yields far from quantitative, if it allows to transform a trivial molecule to a much more elaborated one by a one step procedure. However with a few exceptions[2], most part of the studies described in the literature were performed on aromatic derivatives. Thus plasmochemistry suffers from a lack of knowledge about behaviour of organic molecules submitted to plasma conditions. As a part of our programm on new synthetic methods in Organic Chemistry, we have undertaken studies on capabilities of nonequilibrium plasmas. We wish to report here our first results concerning the behaviour of amines.

Plasmolysis apparatus and operating conditions

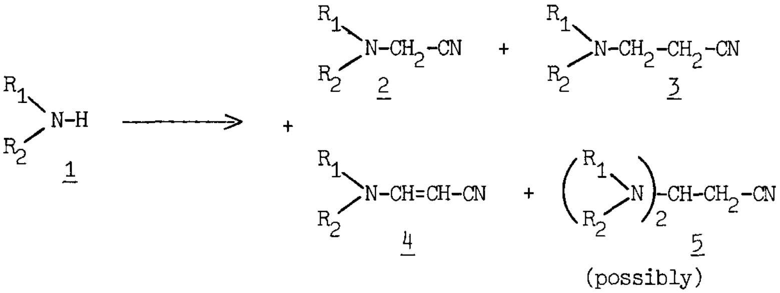
A radio frequency generator[3a] working between 7 to 14 MHz frequencies was used. The power delivered to the plasma may reached 500 Watts and is directly known by mean of a matching network which permits to obtain an efficient coupling of power to the discharge. Reactions were performed in a pyrex glass apparatus[3b] with inductive coupling to the generator[4].

The reaction products were collected on a low temperature trap (cold finger filled up with liquid air) placed immediately behind the inductive coil. Plasma is initially generated at pressure of ca 10^{-2} mmHg ; then the product is distilled in the reaction tube. During the reaction the impedance of the system is monitored in such a way that no return of power to the generator occurs. In these conditions the pressure may reach 1 to 5 mmHg (formation of very low boiling points product like H_2, CH_4, ...). At the end of a plasma reaction, N_2 is admited in the apparatus and the cold finger is allowed to return to room temperature. Gazeous and insoluble polymeric derivatives were discarded. The remaining products isolated by vacuum distillation are mixture of reaction products and unreacted starting material. Yields were calculated in regard to the desappeared starting amine.

Results and discussion

The general reaction observed may be described by Scheme 1.

Scheme 1



It is well known that aminals are generally unstable[5]. Thus we were able to identifie 5 in the crude product of the reaction only when piperidine was plasmolysed. By distillation this aminal leads to the corresponding enamine 4 (R_1, R_2 = $(CH_2)_5$). In the other case aminals were not detected in noticeable amount. We have summarized our main results in the table.

Table

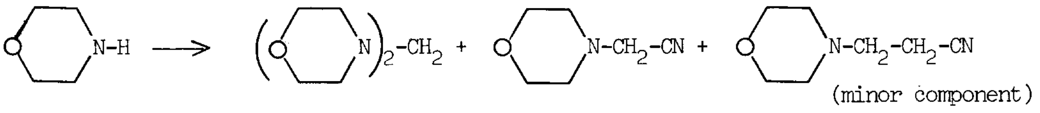
Plasmolysis of amines at power between 230 to 250 W

N°	1		Initial vacuum torr	Reactional vacuum torr	Flow rate g/hr	Starting material recovered %	2 % (a)	3 % (a)	4 % (a)	overall yields %
	R_1	R_2								
1	$(CH_2)_5$		5 10^{-2}	1-1,5	11	22	14	29	57	35
2	$-\overset{\overset{CH_3}{\vert}}{C}H-(CH_2)_3-\overset{\overset{CH_3}{\vert}}{C}H-$		1 10^{-2}	1,5-2	11	10	23	23	54	22
3	$(CH_2)_4$		5 10^{-2}	2,5-3	16	10	27	18	55	22
4	$(CH_2)_2-O-(CH_2)_2$		1 10^{-2}	2,5-3	15	55	50	17	33	30
5	C_2H_5	C_2H_5	5 10^{-2}	4-5	20	30	48	24	28	21

(a) These products were identified on the basis of their[6] IR, NMR and mass spectra for 2 and 3 , by IR, NMR and 2,4-dinitrophenylhydrazone for 4[6].

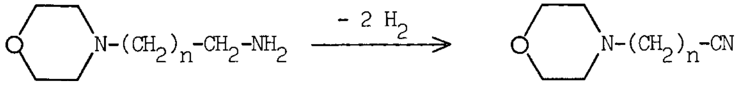
It is noteworthy that the same kind of products are obtained whatever the nature of the starting amine. It is also interesting to note that the plasmolysis of morpholine was performed by GORZNY and MAAHS[2a] ant that their results were somewhat different (Scheme 2).

Scheme 2



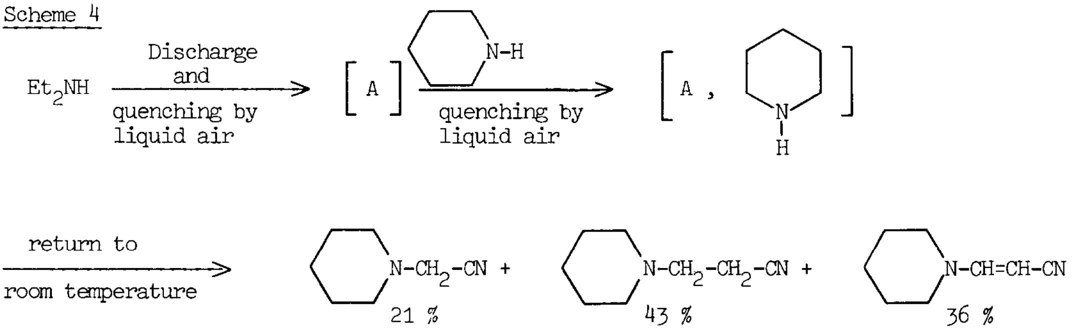
This may be due to the different plasmolysis conditions (they use a 27 MHz generator with capacitive coupling to a quartz glass apparatus) as well as the different trapping conditions. GORZNY and MAAHS interpreted their results in term of condensation inside the discharge of very highly energetic species with morpholine. Moreover they invoked the dehydrogenation of morpholinoamine in the discharge to explain the generation of nitrile (Scheme 3).

Scheme 3



This may be a misinterpretation. Indeed, in the aim to obtain more informations about these reactions, we plasmolysed Et_2NH, quenched as usual and piperidine was then distilled and collected on the cold finger (without plasma). By this procedure, we were able to isolate products similar to those described on Scheme 1 but in which diethylaminogroups were replaced by piperidino ones (Scheme 4).

Scheme 4

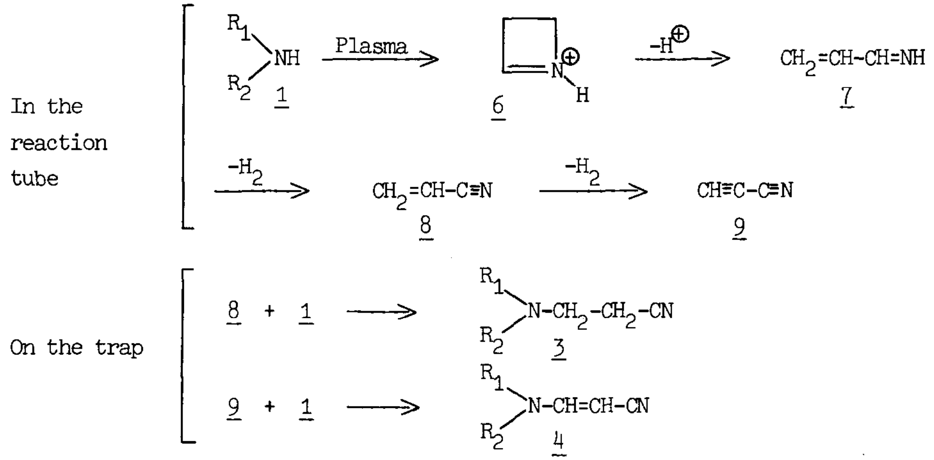


(overall yield 28 % ; flow rate 30 g/hr ; Power 250 W)

This kind of reaction can also be performed by distilling first the piperidine on the cold finger and then plasmolysing the diethylamine. Thus it is clear that in our experiments, highly reactive species [A] does not react with amine in the discharge itself but behind it. These results indicate that it is possible to perform plasma synthesis by reaction of fragments of plasmolysed organic substrates with a non plasmolysed one. Very few reaction of this kind were described in the literature[7].

As usual these reactions may be partially interpreted on the basis of mass spectrometric fragmentation pattern of amines. In this way[8] we suggest the charged specie 6 as the chief intermediate. Thus we propose the mechanism described on Scheme 5 [9].

Scheme 5



The formation of nitrile 2 is more difficult to interprete. The experiment described in Scheme 4 lead to conclude that it is not formed by the mechanism given by GORZNY and MAAHS (Scheme 3), but by condensation of the amine on a highly reactive specie (may be $CH_2=C=\bar{N}^+$) quenched at low temperature.

Conclusion : These first results show that plasmolysis of organic substrates allows unusual synthesis. We are now trying to obtain more informations about these reactions and to improve yields and selectivity.

Acknowledgments : One of us (BF) gratefully acknowledges the Centre National de la Recherche Scientifique, France, for financial aid.

References

1) J.R. Hollahan and A.T. Bell, "Techniques and Applications of Plasma Chemistry", Wiley Interscience (1974)

2) for example : a) K. Gorzny and G. Maahs, Angew. Chem. Intern. Ed., 12, 1004 (1973)
   b) J.G. Huntington and L.L. Miller, J. Am. Chem. Soc., 98, 8101 (1976)
   c) J.H. Kim and E.R. Thornton, J. Am. Chem. Soc., 97, 1865 (1975)

3) a) Generator was constructed in Felden's Laboratory with the technical assistance of M. Masson ; b) Glass apparatus was performed with the technical assistance of M. Vasseur

4) A. Weissberger and B.W. Rossiter "Technique of Chemistry", Vol. I, Part II B, Chapter XI Wiley Interscience (1971)

5) A.G. Cook "Enamines", M. Dekker (1971)

6) J. Shaw, J. Chem. Soc., 1834 (1955)

7) K. Gorzny and G. Maahs, Angew. Chem. Intern. Ed., 12, 1004-1005 (1973)

8) J.H. Beynon, R.A. Saunders and A.E. Williams, "The mass spectra of organic molecules", Elsevier (1968)

9) Addition of amines on cyanoacetylene is well known : S. Murahashi, J. Chem. Soc. Japan, 78, 324 (1957)