Tetrahedron Letters No. 13, pp 1181 - 1184, 1975. Pergamon Press. Printed in Great Britain.

PLASMOLYSIS OF OXAZOLINES, THIAZOLINES, OXADIAZOLES

Larry L. Miller* and John G. Huntington

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

(Received in USA 3 January 1975; received in UK for publication 25 February 1975)

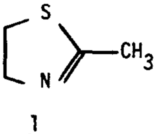
Although it is well known that electrical discharge in an organic vapor produces interesting chemical reactions, only a few attempts have been made to use this phenomenon for organic synthesis. Recent work by Suhr and coworkers,[1] however, indicates that unique and selective discharge reactions are possible and that useful synthetic reactions can be performed

We have initiated an exploratory program in this area utilizing a radio frequency generator as a power supply If sufficient energy is supplied, this produces a continuous discharge The vapor is partially ionized in the process, thus the reactions are promoted by and take place in a plasma. We have found that plasmolysis with this system is often clean[2] and we report here on the fragmentation of several heterocyclic molecules. To our knowledge, pyrrole[1] and morpholine[3] are the only other monocyclic heterocycles that have been studied.

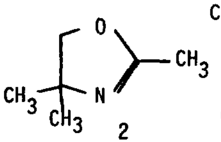
The plasmolysis apparatus was similar to that described by Suhr,[1] using a PM105-B rf generator (International Plasma Corporation) as a source of 13.6 MHz rf energy. This was inductively coupled <u>via</u> copper coils to a 40 mm id pyrex reaction tube The compound to be studied was distilled through the discharge region at a pressure of ca 0.1-0.4 mm Hg and the products collected in a liquid nitrogen trap. Gaseous products were collected in a second trap equipped with a stopcock and analyzed by mass spectroscopy. Product percentages were estimated by glc using a 3/8" X 12', 10% Carbowax 20M/Chromosorb W column, or in the case of compound <u>3</u>, a 12' X 3/8", 15% SE-30/Chromosorb W column at 200°C. A Varian Aerograph Model 90-P gas chromatograph was employed, the peak areas (estimated by the cut and weigh procedure) being uncorrected for thermal conductivity differences.

All compounds were obtained from commercial sources but for compound 3, which was prepared from trans-stilbene episulfide[4] by the method of Helmkamp.[5]

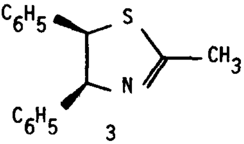
The products resulting from decomposition of compounds 1-4 are shown in Table 1.



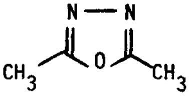
1



2



3



4

Fragmentation to form smaller, stable molecules appears to be general for such compounds.

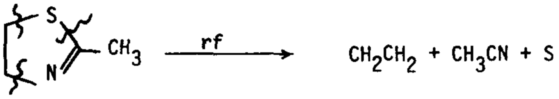


Table 1. Plasmolysis Products

Reactant	Rf Power[a] (Watts)	Pressure (mm Hg)	Flow Rate[b] (mmole/min)	Temperature[c] (C°)	Products, % Yield based on starting material.
1	50	0.1-0.3	0.1	25	ethylene (49), sulfur (51), acetonitrile (51)
2	50	0.1-0 3	0 1	25	$(CH_3)_2C=CH_2$ (30), CH_3CN (32), 2 (60)
3[d]	50	4	0.1	190	E-stilbene (13.7), Z-stilbene (10.1), phenanthrene (4.2)
3[d]	10	4	0.02	190	E-stilbene (31), Z-stilbene (23), phenanthrene (8.1), 3 (32)
4	50	0,1-0.3	0.2	25	CH_3CN (72), 4 (17)
E-stilbene	10	4	0.02	190	Z-stilbene (17), E-stilbene (83)
Z-stilbene	20	4	0.02	190	Z-stilbene (51), E-stilbene (33), phenanthrene (15.4)

---

a) Power produced by the generator. b) Calculated by dividing the quantity of material passed by the time required. c) Temperature of the plasmolysis chamber. For 3, a temperature of 190° was used to prevent condensation in the reaction tube. A control experiment with no plasma demonstrated the compound to be completely stable at this temperature. d) Helium was used as a carrier gas due to the relative nonvolatility of this material.

The sulfur heterocycles are more reactive under these conditions than their oxygen analogs, but the overall course of the reaction is the same in each case. It was also observed that the formation of polymer causes the deviation of the product balance from unity. This phenomenon appears to be less important for the oxygen-containing molecules than in the case of the sulfur compounds, but in either case it can be minimized by judicious choice of pressure and use of low power levels. Increased conversions are achieved if the plasma tube is of large diameter (>40 mm)

The plasmolysis of 2-methyl-cis-4,5-diphenyl-Δ^2-thiazoline (3) was performed in order to examine the stereochemistry of the anticipated stilbene product. The results show the formation of Z and E stilbene as well as phenanthrene, the same products observed when Z or E stilbene is subjected to an RF plasma.[6] Comparison of the ratio of these three prodcuts from Z-stilbene, from E-stilbene, and from thiazoline 3 yields some information about the reaction mechanism. Thus, as shown in Table 1, E-stilbene reacted at 10 watts of power produced no measurable quantity of phenanthrene, whereas thiazoline 3 formed a significant amount. Furthermore, the Z/E ratio is markedly different, being much larger in the thiazoline decomposition. A low-power plasmolysis of Z-stilbene (Table 1) does show the formation of phenanthrene, but the amount of E in the mixture is much less than is formed from the thiazoline.

These data show that the fragmentation does not produce either Z or E stilbene stereospecifically, but instead produces a mixture of isomers. The product ratio is, furthermore, nearly independent of the power over the range 10-50 watts, in contrast to the results from stilbene isomerizations [2,6]

There are a number of mechanisms whereby a mixture of Z and E isomers would be directly produced from the plasmolysis of 3. These include pathways involving diradical and electronically excited intermediates The most appealing possibility is that the fragmentation yields electronically-excited stilbene It is known that this intermediate will produce a mixture of isomers rich in Z product,[7] (and in the gas phase also phenanthrene[8]) whereas other reactions involving ground state stilbene are either stereospecific or form primarily the E product.

The mechanism of the plasmolysis is unknown, but there is apparently no reported analogous photochemical or thermal process Further work addressing the mechanistic questions is in progress.

Acknowledgement This study was supported by the A.P Sloan Foundation through a fellowship to LLM.

References

1. H. Suhr, Angew. Chem. internat. Edit., 11, 781 (1972).
2. Unpublished work of J. G. Huntington.
3. K. Gorzny and G. Maahs, Angew. Chem. internat. Edit., 12, 1004 (1973).
4. R. Ketcham and V. P. Shah, J Org. Chem., 28, 229 (1963).
5. G. K. Helmkamp, D. J. Pettit, J. R. Lowell, Jr., W. R. Mabey and R. G. Wolcott, ibid., 88, 1030 (1966)
6. H. Suhr and U. Schucker, Synthesis, 431 (1972).
7. See for example, G. S. Hammond, et.al, J. Amer. Chem. Soc., 86, 3197 (1964); J. Saltiel and E. C. Megarity, ibid., 94, 2742 (1972), J. Saltiel and B. Thomas, ibid., 96, 5660 (1974)
8. R. Srinivasan, J. Chem. Phys., 39, 580 (1963).