

CYCLIZATION OF 1,4-DIENES IN AN RF PLASMA,  
AN APPARENT Di- $\pi$ -METHANE REARRANGEMENT

Masao Tokuda\* and Hiroshi Suginome  
Department of Chemical Process Engineering  
Hokkaido University, Sapporo 060, Japan

L. L. Miller  
Department of Chemistry, University of Minnesota  
Minneapolis, Minnesota 55455 USA

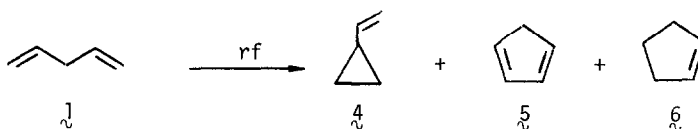
Abstract

1,4-Pentadiene reacted when flowed through a 13.6 MHz gaseous discharge forming vinylcyclopropane, cyclopentene and cyclopentadiene; 3-phenylpropene reacted similarly producing cyclopropylbenzene and indene.

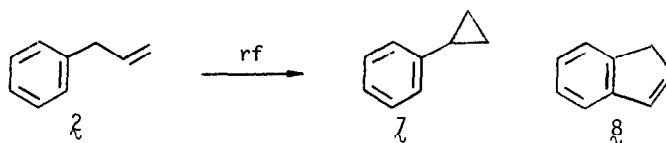
The plasma generated by a radio-frequency discharge provides an unique reaction medium, and therefore the plasmolysis of organic compounds often leads to novel transformations<sup>1</sup> which are not achieved by ordinary chemical methods. In the present investigation we set out to discover photochemical analogues in plasma chemistry. The di- $\pi$ -methane isomerization<sup>2</sup> was chosen as an intriguing and appropriate photochemical reaction, which might be mimicked in a gaseous plasma. Although a variety of complex reactants undergo this photoisomerization, it seemed desirable to begin our search using simple dienes. We report that 1,4-pentadiene and 3-phenylpropene are isomerized by electron impact in the plasma phase. The respective products vinylcyclopropane and cyclopropylbenzene arise from apparent di- $\pi$ -methane isomerizations.

The inductively coupled plasma apparatus used in the present study was very similar to that described previously.<sup>3</sup> The starting 1,4-diene was distilled through the discharge zone produced by an rf generator at 13.56 MHz. Products and unreacted starting materials were collected in a cold trap at  $-70^{\circ}\text{C}$  and were analyzed by GLC. The products were isolated by preparative GLC and identified by spectral means, by comparison with authentic samples. Their yields were determined by GLC with an internal standard.

Plasmolysis of **1** at an applied power of 40W with a flow rate of 3.48 mmol/min converted to 43% of **1** into the products vinylcyclopropane (**4**: 5%), cyclopentadiene (**5**: 21%), and cyclopentene (**6**: 18%). Butadiene, butene, and 1,3-pentadiene were also detected.



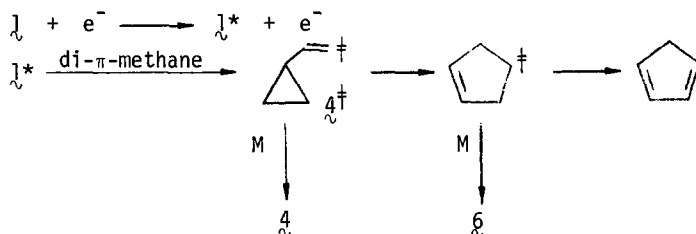
Plasmolysis of **2** gave phenylcyclopropane (**7**) and indene (**8**) as the major products. The formation of small amounts of indan, 1-phenylpropene, cumene, propylbenzene, styrene, toluene, and benzene were also detected. Conversion of **2** and yields of **7** and **8** under various conditions are summarized in Table I. Higher power and lower flow rate gave a higher conversion of **2** and poorer yields of **7** and **8**.



Although products from cyclization<sup>1</sup> and alkene isomerization<sup>1,5,6</sup> are not unusual in plasma chemistry, there is no precedent for the apparent di- $\pi$ -methane reactions forming **4** and **5**. There is a close photochemical analogue.

Mercury-sensitized photolysis of **3** in gas phase has been reported to give **4** and **6** together with other products, without accompanying cyclopentadiene.<sup>7</sup> As far as we are aware, photochemical reaction of **2** has not been reported, although photolysis of *trans*-1-phenyl-2-butene in the gas phase has been reported to give 1-phenyl-2-methylcyclopropane, a product arising from the di- $\pi$ -methane rearrangement.<sup>8</sup> In order to compare the plasma reaction with a photochemical reaction, we carried out the photochemical reaction of **2** in the gas phase (ca. 0.1 mm Hg) with 253.7 nm light. It was found that **3** was formed in a very low yield in this photolysis.

These plasma isomerizations are of synthetic interest, because in contrast to most gas phase photochemistry the reaction is run on the scale of grams. The reaction mechanisms are of intrinsic interest. Following Ocham's rule, we suggest one mechanism which concisely explains the formation of **4**, **5** and **6** from **3**. **3**<sup>\*</sup> is electronically excited and **4**<sup>‡</sup> is vibrationally excited. Reaction with M represents deactivating collisions with other molecules or the wall.



Whatever the mechanism, it is likely that vinylcyclopropane will be initially formed with excess energy and rapidly react further. If it reacted in this way, cyclopentene and cyclopentadiene are the expected products.<sup>9,10</sup>

Some preliminary mechanistic experiments have been performed using **2**. First, in order to confirm whether or not **8** was formed via **3**, the plasmolysis of **3** was attempted. No **8** was formed in this reaction, proving that ground state **3** was not an intermediate in forming **8** from **2**. Second, it should be specifically noted that higher flow rate gives a higher ratio of **7**/**8** (see the three experiments at 30 W in Table 1).<sup>11</sup> The reaction was also studied using 3-phenylpropene-3,3-d<sub>2</sub> (**3**). A di- $\pi$ -methane rearrangement of **3** would produce **9a**. Reactant (**3**) was prepared from methyl phenylpropionate according to the literature procedure.<sup>12</sup> The plasmolysis of **3** afforded a mixture of differently deuterated phenylcyclopropanes (**9**) in the yields shown in Table I. Compositions of **3** and **9** isolated by preparative GLC were analyzed by NMR spectroscopy



and mass spectrometry. The mass spectrum of  $\mathcal{Q}$  proved that it was composed of 21% monodeuterated product and 79% dideuterated product. Analysis of the recovered 3-phenylpropene in this plasma reaction by NMR spectroscopy and mass spectrometry indicated the content of deuterium and the proton ratio of the signals to be the same as those of the starting compound ( $\mathcal{Z}$ ). It thus appears that there are two routes to the apparent di- $\pi$ -methane product  $\mathcal{Q}$ . One route may involve radicals and lead to  $d_1$  product. The major route is a true isomerization, but the presence of the  $d_1$  product makes NMR analysis for the deuteria locations in  $\mathcal{Q}$ - $d_2$  indefinite. The product could contain 1,2-dideuterio-1-phenylcyclopropane, as well as  $\mathcal{Q}_a$  and, therefore, the mechanism for formation of  $\mathcal{Q}$  may not be closely related to the usual di- $\pi$ -methane reaction pathway.

Full details on these and other mechanistic studies will be reported. We emphasize here that new, preparative scale plasma chemistry has been discovered which mimics known reactions of electronically excited molecules. Such isomerizations may prove to be quite general.

Table I. Plasmolysis of 3-Phenylpropene ( $\mathcal{Z}$ ) and 3-Phenylpropene-3,3- $d_2$  ( $\mathcal{Z}$ ).

cmpd	$\underline{P}$ , <sup>a</sup> W	$r$ , <sup>b</sup> $\text{mmol min}^{-1}$	Conversion of $\mathcal{Z}$ or $\mathcal{Z}$ , %	% yield of products <sup>c</sup>	
				$\mathcal{Z}$	$\mathcal{Q}$
$\mathcal{Z}$	15	0.17	91	5	3
		0.43	51	11	6
	30	0.35	90	6	5
		1.35	40	15	10
	45	1.76	36	19	11
		0.71	83	6	7
$\mathcal{Z}$	30	1.44	55	11	11
		1.33	29	25 <sup>d</sup>	10 <sup>e</sup>
	45	1.44	50	15 <sup>d</sup>	9 <sup>e</sup>
		1.77	30	21 <sup>d</sup>	11 <sup>e</sup>

<sup>a</sup>Applied power. <sup>b</sup>Flow rate of the reactant. <sup>c</sup>Based on consumed starting material. <sup>d</sup>A mixture of mono- and di-deuterated phenylcyclopropane ( $\mathcal{Q}$ ). <sup>e</sup>A mixture of indene and mono- and di-deuterated indene.

Acknowledgment. We thank Professor W. E. Farneth for providing authentic samples and information relating to the reaction of vinylcyclopropane. Work at the University of Minnesota was supported by the National Science Foundation.

## References

- (1) (a) Suhr, H., Angew. Chem. Int. Ed. Engl., 1972, 11, 781.  
 (b) Suhr, H., "Techniques and Applications of Plasma Chemistry", Hollahan, J. R.; Bell, A. T., Eds., Wiley: New York, 1974, Chapter 2.
- (2) For a recent review, see Zimmerman, H. E., in "Rearrangements in Ground and Excited States", Mayo, P. de Ed., Academic Press: New York, 1980, Chapter 16.
- (3) (a) Tezuka, M.; Miller, L. L., J. Am. Chem. Soc., 1978, 100, 4201.  
 (b) Tokuda, M.; Miller, L. L.; Szabo, A.; Suhr, H., J. Org. Chem., 1979, 44, 4505.
- (4) The yields shown in the parentheses are based on consumed  $\lambda$ .
- (5) Huntington, J. G.; Miller, L. L., J. Am. Chem. Soc., 1976, 98, 9101. Ibid., Tet. Lett. 1975, 1181.
- (6) Suhr, H.; Schucker, U., Synthesis, 1972, 431.
- (7) (a) Meinwald, J.; Smith, G. W., J. Am. Chem. Soc., 1967, 89, 4923.  
 (b) Srinivasan, R.; Carlough, K. H., Ibid., 1967, 89, 4932.
- (8) Comtet, M., J. Am. Chem. Soc., 1970, 92, 5308.
- (9) Farneth, W. E.; Thomsen, M. W.; Schultz, N. L.; Davies, M. A., J. Am. Chem. Soc., 1981, 102, 4001.
- (10) Crane, D. M.; Rose, T. L., J. Phys. Chem., 1975, 79, 403.
- (11) The dependence of  $\lambda/8$  on flow rate could be explained as pressure effect. Thus, increased flow rates in this reactor<sup>3,5</sup> result in increased pressure at a nearly constant residence time. Increased pressure will tend to cool the electrons and chemically activated products, leading to increase yields of  $\lambda$ . More detailed studies at low conversion are called for.
- (12) Hendrix, W. T.; von Rosenberg, J. L., J. Am. Chem. Soc., 1976, 98, 4850. Final rectification gave 3 over 99% pure (GLC). The NMR spectrum shows no signal due to benzylic proton at  $\delta$  3.40. <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  4.98 (m, 1 H), 5.13 (m, 1 H), 5.99 (m, 1 H), 7.20 (s, 5 H); IR (neat) 3050, 3020, 1625, 1595, 1485, 990, and 605 cm<sup>-1</sup>.

(Received in USA 13 July 1982)