Tetrahedron Letters No.44, pp. 3875-3878, 1969. Pergamon Press. Printed in Great Britain.

STEREOCHEMICAL EFFECTS ON THE MASS SPECTRA OF THE 1,2-DIPHENYLCYCLOBUTANES

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(Received in USA 7 July 1969; received in UK for publication 19 August 1969)

In connection with another study underway in our laboratories, we had occasion to examine the 70 ev mass spectra of both <u>cis</u>- and <u>trans</u>-1,2-diphenylcyclobutane (1). The intriguing differences we observed in these spectra prompted us to examine the mass spectral characteristics of these compounds at lower ionizing potentials as well. We wish to report the results of these investigations in the present communication.

As is commonly observed (2) we find that the <u>cis</u>- isomer fragments with slightly greater facility than the <u>trans</u>- at all ionizing potentials investigated, although this difference is small, with the <u>trans</u>- molecular ion (m/e 208) accounting for 10.5% of the total ion current at the lowest potential studied <u>vs</u>. 7.7% for the <u>cis</u>- isomer at the same voltage. The base peak in both cases under all the conditions was at m/e 104. While there were, as expected, few important differences at lower m/e ratios, significant differences in abundances of peaks appearing at 180, 118 and 117 were found. A summary of the data appears in Table I.

From a study of the data in Table I, several facts clearly emerge. The notable differences in the spectra of the two compounds are the following: 1) for the <u>cis</u> isomer, the only important primary fragmentation process (other than that leading to the 104 ion) is one which yields an ion at m/e 180; 2) in the <u>trans</u>- compound, on the other hand, a major primary fragmentation gives ions of m/e 118 and relatively fewer of the 180 ions than the <u>cis</u>-; 3) the low voltage results greatly accentuate these differences and remove the obscuring effect of the secondary fragmentations and less important primary fragmentations which are found when higher voltages are used.

Table I

MASS SPECTRA OF CIS- AND TRANS-1,2-DIPHENYLCYCLOBUTANE[a,b]

	70 ev		19.4 ev		11.7 ev		9.1 ev	
m/e	cis	trans	cis	trans	cis	trans	cis	trans
51	3.5	2.0	-[c]	-	-	-	-	-
63	1.4	1.2	-	-	-	-	-	-
65	1.2	1.3	-	-	-	-	-	-
76	1.7	1.3	-	-	-	-	-	-
77	8.7	3.8	2.7	0.2	0.3	-	-	-
78	7.1	6.5	3.3	1.2	1.4	0.6	0.8	0.6
89	1.5	1.8	-	-	-	-	-	-
91	2.5	3.6	1.1	1.2	0.6	0.4	-	0.2
92	0.6	4.5	0.8	0.5	0.7	0.5	-	0.4
102	1.6	1.2	-	-	-	-	-	-
103	6.5	5.4	2.7	0.8	1.0	0.1	-	-
104	45.1	56.5	77.6	85.6	79.7	86.0	81.3	84.5
115	1.1	1.4	0.3	0.3	-	-	-	-
117	0.3	1.3	0.6	1.6	0.3	1.0	-	0.7
118	< 0.1	0.8	0.3	1.5	0.3	2.2	-	2.5
165	1.7	1.0	0.8	0.3	0.6	-	-	-
176	0.4	0.4	-	-	-	-	-	-
177	0.3	0.3	-	-	-	-	-	-
178	2.1	1.7	0.8	0.2	-	-	-	-
179	2.5	1.2	1.9	0.7	1.3	0.1	0.8	-
180	2.5	0.8	3.5	0.8	6.5	0.7	9.4	0.6
208	1.6	2.2	3.5	5.2	6.6	8.5	7.7	10.5

a) Ion abundances expressed as percentages of the total ion current. Spectra were obtained with a Hitachi RMU-6D double focussing mass spectrometer.

b) This is not a complete list of all peaks.

c) Undetected.

Consideration of these differences leads to a number of alternate explanations for the dramatic dichotomy in the behavior of cis- and trans-1,2-diphenylcyclobutane. An intriguing possibile explanation for the loss of a mass 28 fragment from the cis- compound to yield m/e 180 ion is the formation of the dihydrophenanthrene radical-ion outlined in Figure 1. This would account nicely for the much lower abundance of this ion found in the spectrum of the trans- isomer. Such a suggestion can be supported by the report that stilbene, upon electron impact, yields this same ion (3). Consistant with this is the observation that 180 → 165 does occur (m* 151.2).[†] While the timing is uncertain, the loss of CH_3 suggests the possibility that, initially, the decomposing 180 ion possessed the dihydrophenanthrene structure. Alternately, a concerted loss of stilbene from the molecular ion could be envisioned. If this were the case, it would appear that one would have to propose a disrotatory ring opening to account for the favored formation from the cis- cyclobutane.

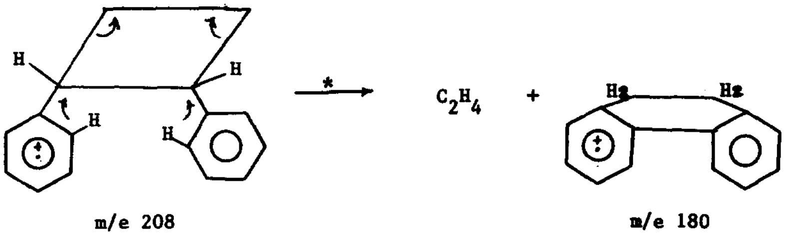

Figure I. Formation of the m/e 180 ion from cis-1,2-Diphenylcyclobutane

The formation of the 104 ion requires comment. This ion probably arises via a concerted process, since it would seem that a stepwise fragmentation preceeded by simple bond cleavage would lead to a loss of stereochemical integrity and thus, identical spectra for the isomers. This process is, at least in part, analogous to thermal decompositions of neutral species since an abundant metastable ion (m* 52.0) is observed for the transition 208 → 104 (4). This would seem to be in violation of the Woodward-Hoffmann rules, which predict 2 + 2 cycloadditions to be thermally non-allowed (5).[††]

The loss of C_7H_6 (a novel loss indeed) to give the 118 radical-ion was established by observation of the metastable for this transition (m* 66.9). This is a far more important process in the fragmentation of the trans diphenylcyclobutane than for its cis- isomer. This lack of important

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[†] All metastables were obtained in the defocussed mode by an electrostatic sector scan (6).

[††] Unless, of course, inversion at two of the carbons is allowed.

amounts of m/e 118 ions in the cis- case suggests that the concerted process in the cis-1,2-diphenylcyclobutane is more easily accomplished. Therefore, the relatively higher energy process leading to 118 cannot compete favorably.

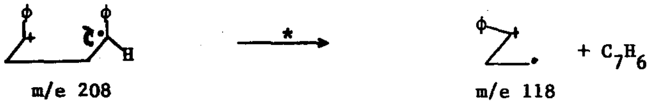

Figure II. Formation of the 118 ion.

In conclusion, this work demonstrates once more the utility of mass spectra obtained at low ionizing voltages for the purpose of detecting differences in the mass spectral behavior of geometric isomers. For one of the two isomers studied in the present investigation, it appears that we have observed either an unusual rearrangement to yield a dihydrophenanthryl radical-cation or an equally unusual concerted elimination to yield the stilbene radical-ion. In both isomers we find an apparent concerted reaction which yields the 104 ion. We hope to establish the structures of the ions by further studies, using ion cyclotron resonance techniques, which are currently underway. Our results suggest that further mass spectrometric investigations of isomeric cyclobutanes may provide a means for establishing otherwise difficult stereochemical assignments.

Acknowledgements. We wish to gratefully acknowledge the Petroleum Research Fund of the American Chemical Society for grants to M.L.G. and C.L.W. in partial support of this research. One of us (C.L.W.) thanks the Research Council of the University of Nebraska for its generous support. We are especially grateful to Professor R. M. Dodson for his generous gift of a sample of 1,2-diphenylcyclobutene.

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