

PHOTOCHEMICAL ANALOGIES IN MASS SPECTRA. THE EPOXYCYCLOPENTENONE-PYRONE REARRANGEMENT

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(Received 7 April 1967)

Similarities between the photochemical behavior of certain organic compounds and their preferred modes of fragmentation on electron impact have been noted before; the outstanding example is the McLafferty rearrangement (1), which bears a marked similarity to the Norrish Type II photochemical decomposition of ketones and other species (2). The similarity of ortho hydrogen abstraction by the nitro group by ultraviolet irradiation and upon electron impact has been discussed (3). The expulsion of carbon monoxide from ketones under both sets of conditions is another example that furnishes support for the contention that the two chemistries have sufficient interrelation to be of predictive value in either case (4).

We report here a remarkable example of formation of almost identical populations of states in molecular ions from two photochemically related compounds, 4,5-diphenyl-2-pyrone (I) and 3,4-diphenyl-4,5-epoxy-2-cyclopenten-1-one (II). The conversion of the latter compound into the former by light of wavelength greater than 2800 Å has been examined in detail (5,6). The mass spectra obtained by direct insertion of samples into the source of a Hitachi RMU-6E mass spectrometer at 40° (Table I) are nearly identical; the only significant differences are a somewhat less abundant molecular ion, and more abundant ions at m/e 77 and m/e 105, in the spectrum of the epoxyketone. In addition, the metastable ion transitions in each spectrum, which serve as guideposts in identifying the structures of ions (7), are quite similar in position, intensity, shape, and, in the case of "flat-topped metastable ions," (8,9) amount of excess energy released (Table II). It is tempting to suggest that removal of an electron from the epoxyketone produces the same effect as promotion of an electron to an excited state, that is, rearrangement to the pyrone,

TABLE I
Mass Spectra of 4,5-Diphenyl-2-pyrone (I) and 3,4-Diphenyl-4,5-epoxy-2-cyclopenten-1-one (II)

m/e	relative intensity		m/e	relative intensity		m/e	relative intensity		m/e	relative intensity	
	I	II		I	II		I	II		I	II
18	4	3	81	2	1	113	4	4	176	3	5
27	2	3	81.5	3	3	114	8	9	177	2	2
28	9	9	82	4	4	115	9	13	178	7	11
29	2	1	82.5	11	13	116	1	1	179	2	5
32	2	1	83	4	5	124	4	4	187	4	3
38	9	10	86	2	3	124.5	1	1	188	4	3
39	1	1	87	4	5	125	1	1	189	31	38
41	1	1	88	5	5	126	3	3	190	12	14
43	2	2	89	9	12	139	4	5	191	75	89
44	2	2	90	2	3	142	2	2	192	29	37
50	4	5	91	1	1	149	1	2	193	4	4
51	8	14	93.5	2	2	150	2	2	201	1	1
52	2	3	94	4	5	151	2	2	202	2	3
57	1	1	94.5	13	15	152	2	2	203	2	3
62	4	4	95	7	9	163	5	6	204	1	1
63	11	15	95.5	4	5	164	2	3	205	4	4
64	2	2	96	4	5	165	18	21	206	1	1
65	4	4	101	4	5	166	2	3	218	2	2
69	1	1	101.5	1	1	170	2	1	219	13	14
69.5	2	3	102	3	6	102.5	1	1	220	75	89
74	4	5	103	2	2	105	4	23	221	13	16
75	4	5	106	4	2	106	2	2	222	1	1
76	4	6	109	3	3	109	3	3	230	8	13
77	8	16	109.5	1	1	109.5	1	1	231	4	5
78	1	3	110	3	3	110.5	1	1	232	1	1
			110.5	1	1	111	1	1	247	15	15
			111	1	1				248	100	100
									249	18	18
									250	2	2

TABLE II
Intensities of Metastable Transitions

Position		Assignment	Excess Energy	Intensity Relative to Precursor	
Calcd.	Found			pyrone	epoxyketone
246.0	246.0	248 → 247	--	0.9%	0.8%
218.0	218.0	220 → 219	--	a	a
213.2	213.0	248 → 230	0.8 ev	0.1%	0.1%
195.3	195.4	248 → 220	0.17 ev	0.4%	0.5%
187.1	187.5	191 → 189	--	1.3%	1.4%
167.0	{ 166.0	220 → 191	--	0.9%	0.7%
	{ 167.4	220 → 192	--		
142.5	142.5	191 → 165	0.28 ev	0.6%	0.5%

(a) The shape of the metastable ion is sharp, and there is a small normal peak at its apex, so that measurement of its height is impractical. It appears to be of similar size in each spectrum.

but obviously there is no guarantee that the skeleton of the pyrone remains unaltered on electron impact. The fragmentation pattern can be fitted easily to the pyrone structure (10,11), however, as shown in Figure 1. In addition, the formation of the ion of m/e 105 in greater abundance by

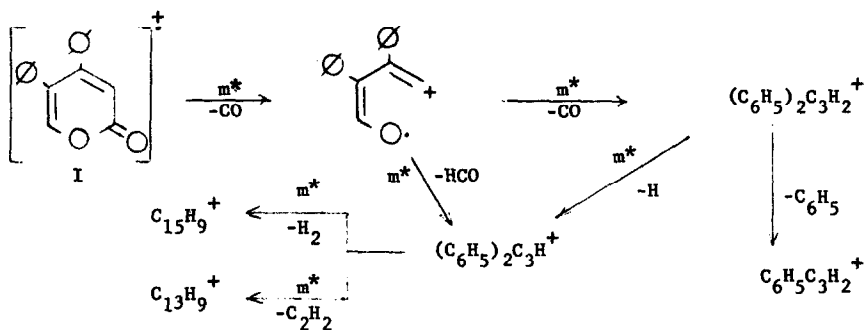


FIG. 1

the epoxyketone may be rationalized by the assumption that not all the epoxyketone molecules attain the same distribution of structures as the pyrone, but that a few may fragment as Figure 2.

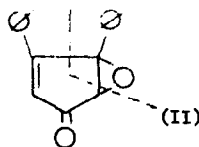


FIG. 2

It is no longer surprising to find that a number of hydrocarbons produce the same ion distribution in the mass spectrometer; for example, the spectra of anthracene, phenanthrene, and diphenylacetylene are nearly the same (14). In fact, the similar spectra of hydrocarbons have been the subject of many elegant studies -- isomers of C_8H_8 (15), C_8H_6 (16), C_8H_4 (17), $C_{10}H_8$ (18), and particularly C_7H_8 (19) are noted examples. The isomerization of systems containing electronegative atoms is, on the contrary, much less thoroughly explored, for in general well-established fragmentation patterns directed (20,21) by the usual functional groups are sufficient to rationalize the spectra of these compounds. The present example would indicate that the juxtaposition of functional groups capable of effective electronic interaction may produce unexpected rearrangements, and that a familiarity with photochemistry is helpful in interpreting the mass spectra of compounds with such systems.

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