THE ULTRAVIOLET SPECTRA OF A SERIES OF FULVENES

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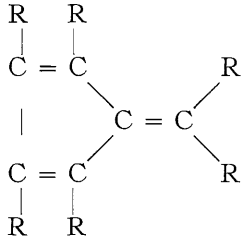
Fulvenes were first prepared by Thiele (1900) by the alkaline condensation of cyclopentadiene with various ketones and aromatic aldehydes. Fulvenes are highly colored and are characterized by an interesting kind of multiply conjugated double bonds:



The R groups may be hydrogen, alkyl or aryl groups. The parent compound, fulvene itself, in which all the R's are hydrogen, has not been successfully prepared in spite of occasional literature references to it. Sklar (1937) refers to dimethyl fulvene incorrectly as fulvene itself. Wheland (1941) and Pullman, Pullman and Rumpf (1948) refer to calculations for the hypothetical compound fulvene, though the non-existence of the substance is not apparent from their papers.

There has been no systematic study of the absorption spectra of the unsubstituted cyclopentadiene derived fulvenes. In spite of the fact that there are potentially as many such compounds as there are aldehydes and ketones combined, not more than a dozen simple fulvenes with aliphatic groups (in the 6, 6 position) have been previously reported, and of these, fulvene and methyl fulvene have not been isolated. The highly arylated fulvenes and those derived from indene and fluorene have been more thoroughly studied.

EXPERIMENTAL

The fulvenes were prepared by the method of Thiele (1900), except the cyclopentylidene cyclopentadine and cyclohexylidene cyclopentadiene; which were made by the method of Kohler and Kable (1935). The furfurylidene cyclopentadiene was best purified by ether extraction followed by recrystallization from petroleum ether.

Ultraviolet and visible absorption spectra were obtained using the Beckman D U spectrophotometer. A standard solution in absolute methanol was made of each fulvene, and that solution diluted quantitatively until the fulvene concentration was low enough to permit optical density measurements over the desired range.

Refractive indices were measured with an Abbe refractometer, using daylight. Approximate molecular weight determinations were made cryoscopically in benzene solution with a Beckman melting point apparatus and usually agreed within 2 percent of theoretical. This check was made partly to determine purity and partly to make sure that there was no accumulation of polymerization or oxidation products. All measurements were made as quickly as possible on freshly prepared material.

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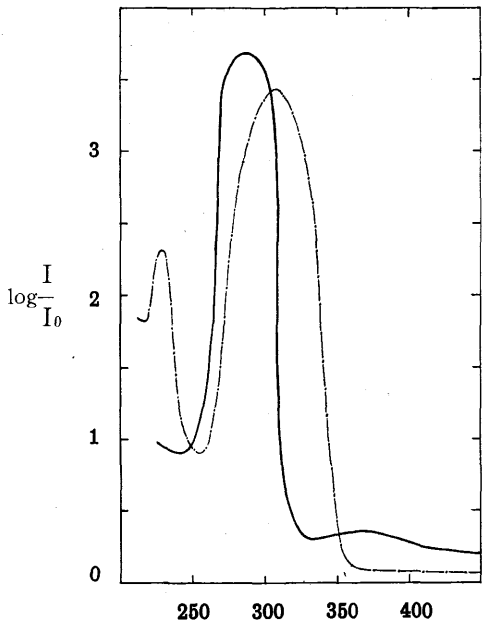

FIGURE 1. The optical density D log I/I for dimethyl fulvene (solid line) and phenyl fulvene, plotted against wave length in microns. Solutions of the fulvenes were 0.00008 M in absolute methanol.

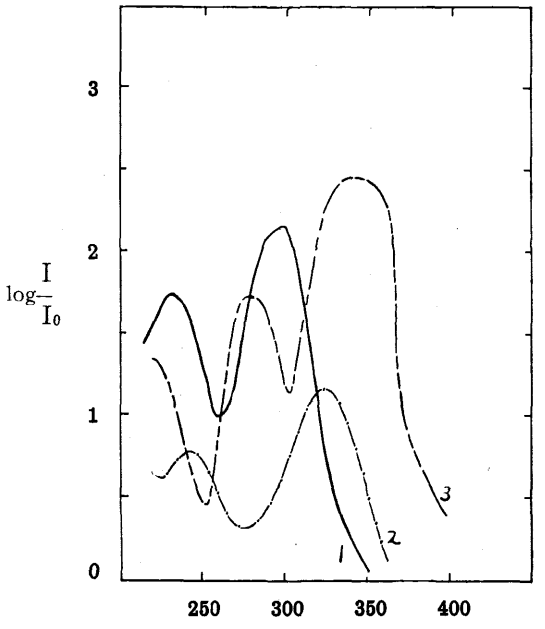

FIGURE 2. The optical density D log I/I plotted against wave length in microns for methyl phenyl fulvene (solid line), diphenyl fulvene (dotted line), and furfurylidene cyclopentadiene (dash line). Solutions were 0.00005 M in absolute methanol.

RESULTS

Some physical properties for eleven fulvenes are tabulated in table 1. Methyl n-amyl fulvene has not been previously reported. (Calc. C 88.82%, H 11.18%. Found: C 88.76%, H 11.34%) Our data for the other compounds are given because they are supplementary to the data in the literature or are valuewise different.

Methyl n-amyl fulvene is an orange colored oil which slowly hardens in air and is quite similar in appearance, odor and behaviour to the other simple fulvenes.

TABLE 1

Physical constants of a series of fulvenes.

Compound	Boiling Point		Refractive Index	Color
	Our Data	Literature		
dimethyl fulvene[1-2]	66–68 (25 mm) 156–158 (760 mm) −13 (melting pt.)	46 (11 mm) 153–154 (717) about 4	1.5338	Yellow-orange
methyl ethyl fulvene[2-3]	67– 70 (25 mm) 165–166 (760 mm)	62.5 (13 mm)	1.5423	Yellow-orange
methyl n-propyl fulvene [4]	177–178 (760 mm)	61–63 (9 mm)	1.5245	Orange
methylisopropyl fulvene[5]	181–182 (760 mm)	67–68 (10 mm)	1.5292	Orange
methyl n-amyl fulvene	213–214 (760 mm)		1.5166	Orange
cyclopentylidene cyclopentadiene [6]	80–82 (25 mm)	55–57 (2 mm)	1.5472	Yellow
cyclohexylidene cyclopentadiene[6]	80–83 (25 mm)	78–80 (25 mm)	1.5474	Yellow
furfurylidene cyclopentadiene	70–72 (25 mm)		1.5845	Orange
phenyl fulvene [1]	3 to 5 (melt.)	about 31	1.5541	Deep red
methyl phenyl fulvene[1]	147–151 (25 mm)	130.5 (10.5 mm)	1.5596	Red oil
diphenyl fulvene[1]	81 (melt. pt.)	82 (melts)		Crimson plates

[1]Thiele (1900). [2]Thiele and Balhorn (1906). [3]Engler and Frankenstein (1901). [4]Halpern (1943). [5]Kazanskii and Gokhanov (1949). [6]Kohler and Kable (1935).

The characteristic absorption spectrum of the fulvene molecules displays a strong absorption peak at 265–271 mu and a weaker absorption peak between 352 and 360 mu. The spectra are virtually identical for dimethyl fulvene, methyl ethyl fulvene, methyl n-propyl fulvene, methyl isopropyl fulvene, methyl n-amyl fulvene, cyclopentylidene cyclopentadiene and cyclohexylidene cyclopentadiene. The absorption peaks shift slightly toward longer wave lengths as the size of the molecule is increased. Stark and Steubing (1908) report strong absorption bands for dimethyl fulvene at 270 and 365 mu, which differs slightly from our data.

The conjugation of the fulvene group at the 6 position with one phenyl group shifts the maximum absorption peak about 30 mu toward the longer wave lengths and decreases the absolute amount of absorption. The conjugation of the fulvene

with two phenyl groups in the 6 position shifts the maximum absorption peak about 25 mu more. A new peak at 230–245 mu is seen in these phenyl fulvenes, which may correspond to a similar peak in the other fulvenes which is below the range of the instrument. In these phenyl fulvenes, the small absorption peak at around 360 mu is no longer found.

Furfurylidene cyclopentadiene exhibits a curve somewhat similar to that of diphenyl fulvene, with a further shift in the maximum absorption peak of about 20 mu.

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