The Fundamental Fragmentation of Several Fulvenes upon Electron Impact

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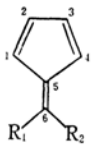
A few papers have appeared concerning the mass spectral fragmentation patterns of non-benzenoid aromatic compounds.[1,2] Here we will report, in a preliminary form, as the behavior of several simple fulvene derivatives upon electron impact.

The fragmentation of 6-methylfulvene by electron impact was first observed by Hanus and Dolejsek[3] in relation to their study of the series of hydrocarbons which have the molecular formula of C_7H_8, e. g., toluene, cycloheptatriene, spiro-[2, 4] - heptadiene - 2, 4, ethinylcyclopentene - 1, ethinylcyclopentene-2, etc. The most important step of the fragemtation is the formation of the tropylium ion by the expulsion of hydrogen from the molecular ion. The feature is common to all of the C_7H_8 isomers.



(1) : $R_1=R_2=CH_3$
(2) : $R_1=CH_3$, $R_2=C_2H_5$
(3) : $R_1=CH_3$, $R_2=CH_2CH(CH_3)_2$
(4) : $R_1-R_2=(CH_2)_5$
(5) : $R_1=H$, $R_2=C_6H_5$
(6) : $R_1=CH_3$, $R_2=C_6H_5$
(7) : $R_1=R_2=C_6H_5$

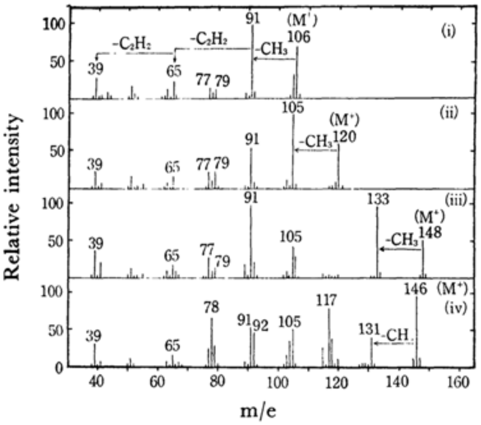
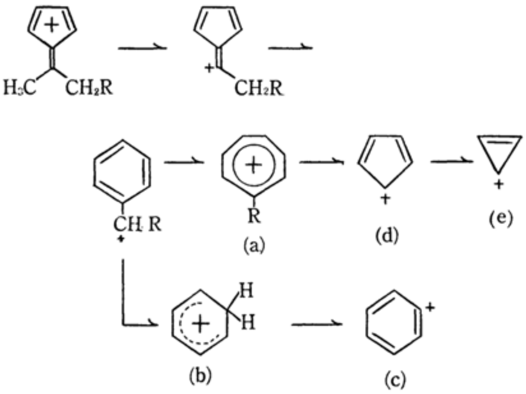


Fig. 1. Mass spectra of 6, 6-dialkylfulvenes.
(i) 6, 6-Dimethylfulvene
(ii) 6-Methyl-6-ethylfulvene
(iii) 6-Methyl-6-isobutylfulvene
(iv) 6, 6-Pentamethylenefulvene

In the mass spectra of the 6, 6-dialkyl derivatives, such as dimethyl- (1), methyl-ethyl- (2) and methyl-isobutylfulvene (3) [see Fig. 1], the base peaks [*m/e* 91, 105, and 133] produced by the elimination of a fragment of 15 mass units from the corresponding parent ions may safely be assumed to be the tropylium, methytropylium, and isopropyltropylium ions (a: R=H, CH_3, i-C_3H_7) respectively. The formation of these ions is probably associated with the loss of the methyl radicals from the 6-position of the fulvenes. In the low mass region of the spectra of these fulvenes, a group of peaks, *m/e* 79, 77, 65 and 39, is characteristic of all isomers of the hydrocarbons of C_7H_8; the peaks may reasonably be interpreted as indicating the ions of benzonium (b), phenyl (c), cyclopentadienyl (d), and cyclopropenylium (e) respectively.



(1′) : R=H
(2′) : $R=CH_3$
(3′) : $R=CH(CH_3)_2$

6, 6-Pentamethylenefulvene (4), however, showed a peculiar fragmentation pattern. In spite of the fact that compound 4 has no methyl substituent on the 6-position, the first step of the fragmentation is the loss of a methyl radical [*m/e* 131, M^+-15]. The process is confirmed by the existence of an appropriate metastable ion peak at *m/e* 117.5. This suggests that the first step of the fragmentation is the well-known β-fission of the aliphatic moiety, with a simultaneous expulsion of the methyl radical, thus leading to the ion of *m/e* 131 (f). The mechanism of the appearance of peaks at *m/e* 92 and 78 [Fig. 1, (iv)] with a considerable intensity still remains in question.

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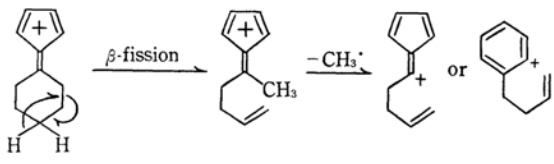


(4′) (f)

The base peaks from 6-phenyl- (5) and 6-methyl-6-phenylfulvene (6) [see Fig. 2] are ions of *m/e* 153 (g); they correspond to the loss of the hydrogen and the methyl radicals $[M^+-1$ and $M^+-15]$ respectively.

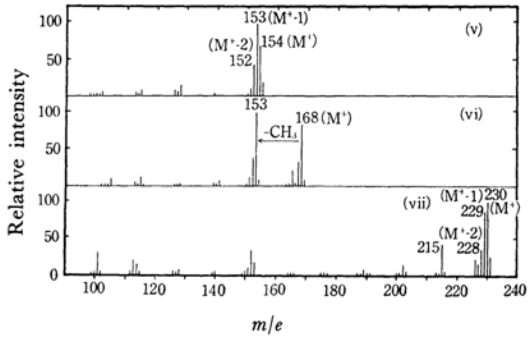
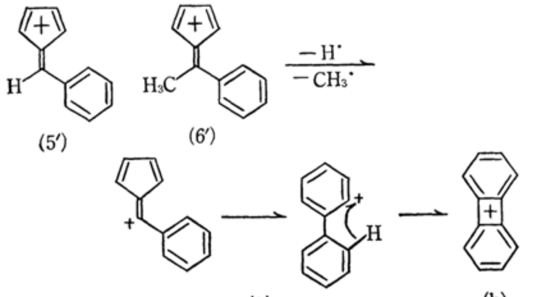


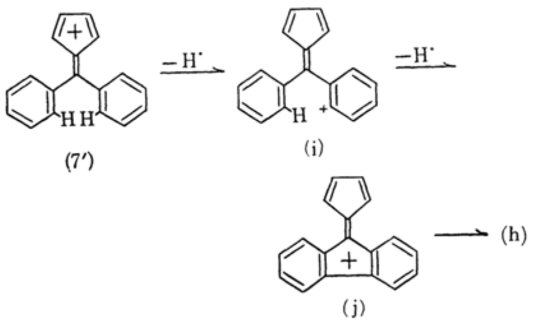
Fig. 2. Mass spectra of 6-arylfulvenes.
(v) 6-Phenylfulvene
(vi) 6-Methyl-6-phenylfulvene
(vii) 6,6-Diphenylfulvene

The moderately intense peak at *m/e* 152 in both compounds is presumably a biphenylene ion (h) produced by the further loss of hydrogen. This is supported by the fact that the spectra in the low mass region [less than *m/e* 153] of the compounds 5 and 6 were similar to that of biphenyl.



(5′) (6′) (g) (h)

6,6-Diphenylfulvene (7) does not show any tendency to eliminate the phenyl radical from the 6-position, but it does show very intense peaks at *m/e* 229 $[M^+-1]$ (i) and at *m/e* 228 $[M^+-2]$ (j). In this case, the interaction of two stericallycrowded phenyl groups probably plays an improtant role in the fragmentation process of this compound. Thus, the formation of a $[M^+-2]$ ion through an intramolecular abstraction of a hydrogen atom from the ortho position of the phenyl group is conceivable. This $[M^+-2]$ ion may naturally by represented as a dibenzofulvalene ion (j). Furthermore, the prominent metastable ion peak at *m/e* 101.5 suggests that the next fragmentation step is the formation of the biphenylene ion.



(7′) (i) (j)

Finally, it should be pointed out that the most fundamental fragmentation of 6-substituted fulvenes is initialed by the fission of hydrogen or substituents at the 6-position, thus forming stable aromatic ions except in the case of 6,6-diphenylfulvene (7).

The mass spectra were taken with a Hitachi Mass Spectrometer, Model RMU-5B, using an all-glass inlet system. The ionizing potential was kept at 75 eV., and the ionizing current, at 80 μamp.

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