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FURTHER INSIGHT INTO THE MASS-SPECTRAL FRAGMENTATION OF TETRACYCLONE. TETRAPHENYLTETRAHEDRANE ION

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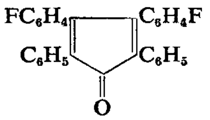
Abstract—The *p*-fluoro labeling technique is used to demonstrate that the ions formed by the loss of CO from tetracyclones pass through a tetrahedral transition state or intermediate before they fragment.

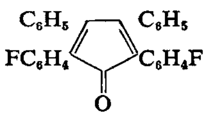
ISOTOPIC labeling techniques have a well established place in the determination of reaction mechanisms in mass spectrometry.[1] As a result of earlier studies on substituent effects,[2,3,4] we have recently suggested that the *p*-fluoro substituent may be used as a label in a similar fashion to the use of isotopes for the study of compounds with aromatic rings attached to the reaction center.[5] It was shown that the *p*-fluoro substituent gives scrambling data quantitatively similar to those obtained by deuterium labeling when the substituted phenyl ring does not interact directly with the reaction site, and has the advantages of commercial availability in many forms, low cost, complete incorporation, and wide separation of the *m/e* ratios of fragment ions and accompanying metastable peaks.

Applying this technique to the structure of the $[M - CO]^{+\cdot}$ ion from the labeled tetracyclone 3,4-bis(*p*-fluorophenyl)-2,5-diphenylcyclopentadienone (I), we showed that this ion must have a cyclic structure, because $C_{14}H_{10}^{+\cdot}$ is produced from the $[M - CO]^{+\cdot}$ ion, as are $C_{14}H_9F^{+\cdot}$ and $C_{14}H_8F_2^{+\cdot}$. However, the ion cannot be of square symmetry, which would demand a distribution of 1:2:1 in the amount of unfluorinated, monofluorinated and difluorinated products formed. The distribution actually observed was 1:3·1:0·89 for the metastable ions related to the decompositions to these respective products. It was therefore necessary to postulate that distortion from square symmetry, as in a rectangle, or else a new symmetry, as in the tetrahedron, was present. We now report results which in the first place demonstrate that the label distribution found is not unique to the substitution pattern used in I, and more significantly that the structure actually requires interpretation in terms of tetrahedral symmetry.

The compounds chosen for study were two further isomers of I containing the fluorine labels at different positions, 2,5-bis(*p*-fluorophenyl)-3,4-diphenylcyclopentadienone (II) and 2,4-bis(*p*-fluorophenyl)-3,5-diphenylcyclopentadienone (III). These were prepared in two steps and four steps respectively from commercial starting



(I)



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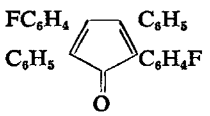
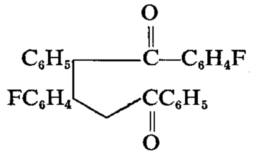


(III)

materials by straightforward routes with ample precedent in the literature. To prepare II, the calcium salt of *p*-fluorophenylacetic acid was pyrolyzed and the resulting 1,3-bis(*p*-fluorophenyl)propanone-2 condensed with benzil. To prepare III, 4-fluorochalcone (from *p*-fluorobenzaldehyde and acetophenone) was condensed with 4′-fluoro-2-phenylacetophenone to yield the 1,5-diketone (IV). This was internally pinacolized and dehydrated to give the cyclopentadiene (V), which was oxidized to III. Further details and references are given in the experimental section.



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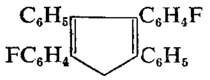
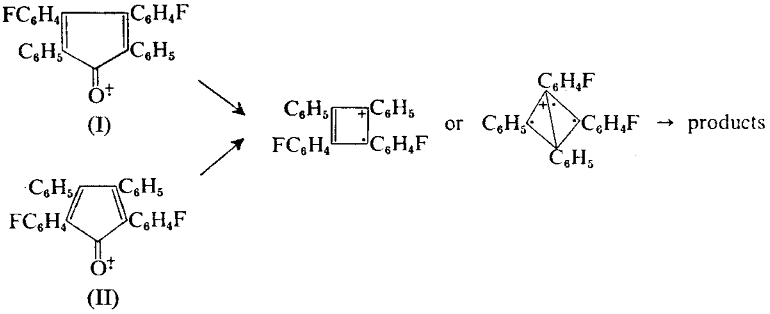


(V)

The mass spectrum of II should resemble that of I very closely if a closed structure for the [M − CO]$^{+\cdot}$ ion is present (eqn. 1). Data for compound I are reproduced from the earlier study and new data for II from a cold direct-insertion probe* are given in Table 1. These clearly indicate that the intermediates in the decompositions are quite similar in structure. Any attempt to use the relative intensities of these normal peaks for further quantitive interpretation is unwarranted, however. These numbers represent complex ratios of rates of formation and decomposition, and in addition may also reflect contributions to the ion populations by other different pathways. Any correspondence in the ratios of these intensities to whole numbers would be coincidental, and they should also be different from the ratios of the



(1)

TABLE 1. RELATIVE INTENSITIES OF NORMAL PEAKS IN THE MASS SPECTRA OF I AND II.

m/e	Assignment	Rel. intensity, I	Rel. intensity, II
420	$M^{+\cdot}$	100	100
392	$[M - CO]^{+\cdot}$	32	33
214	$C_{14}H_8F_2^{+\cdot}$	15	17
196	$C_{14}H_9F^{+\cdot}$	89	97
178	$C_{14}H_{10}^{+\cdot}$	29	35

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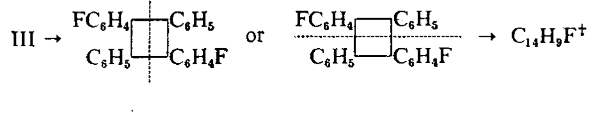
* Similar relative intensities were obtained at temperatures of 250° to 260°. The data from our earlier paper were taken from a spectrum of compound I recorded at 270°, and it was noted that this spectrum was also essentially temperature-invariant. Combined, the data illustrate the invariance of relative intensities with temperature and indicate the absence of pyrolytic contributions.

metastable intensities, because of the small effect of F on decomposition rates.[3] Of greater importance for quantitative interpretation are the relative values of the integrated metastable intensities on a linear *m/e* scale, for these represent only rates of formation of each product from a common precursor, except in those rare cases[6] where consecutive decompositions occur in the field-free region. These data for the two isomers are given in Table 2. They suggest very strongly that the same intermediate is attained in both decompositions, as must be expected on the basis of a symmetrical closed structure for the intermediate. The close similarity of the data suggest that for II, as for I, a rectangular or distorted tetrahedral structure can explain the fragmentation of the $[M - CO]^{+\cdot}$ ion, and that for the *p*-fluoro substituent $\log Z/Z_0^2$ equals $-0{\cdot}02$, a value whose absolute value is so small that the fluorine atom acts as a 'dead' label.[5]

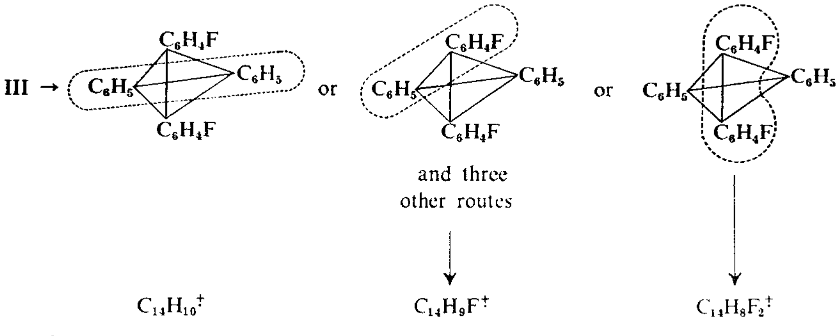
TABLE 2. RELATIVE INTEGRATED INTENSITIES OF CHARACTERISTIC METASTABLES FOR I AND II.

m/e, found	assignment	*m/e*, calcd.	rel. intensity, I	rel. intensity, II
81·0	392 → 178	80·8	1	1
98·0	392 → 196	98·0	3·1	3·2
117·0	392 → 214	116·8	0·89	0·93

In order to resolve the question of the symmetry of the intermediate, we examined the spectrum of compound III. If the $[M - CO]^{+\cdot}$ ion from III is square or rectangular (or even acyclic) then it can decompose only to give an ion of *m/e* 196 and a supporting metastable at *m/e* 98·0 (eqn. 2); but if a tetrahedral structure is formed, then all three 'diphenylacetylene' fragments should be formed as it decomposes (eqn. 3). From eqn. 3, the ratio of intensities would be 1:4:1. The actual results



(2)



(3)

obtained for the normal and metastable peaks in this spectrum from a cold probe are given in Table 3. By inspection, a tetrahedral form *must* be present. Once again the ratio (1:5·2:0·87) suggests that the structure is not symmetrical, or conceivably that a mixture of structures is present. However, the absence of significant temperature

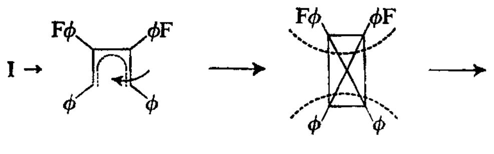
TABLE 3. PERTINENT NORMAL AND METASTABLE PEAKS IN THE MASS SPECTRUM OF COMPOUND III.

m/e	assignment	rel. intensity
420	$M^{+\cdot}$	100
392	$[M - CO]^{+\cdot}$	35
214	$C_{14}H_8F_2^{+\cdot}$	7
196	$C_{14}H_9F^{+\cdot}$	80
178	$C_{14}H_{10}^{+\cdot}$	13
81·0	392 → 178	1·0*
98·0	392 → 196	5·2*
117·0	392 → 214	0·87*

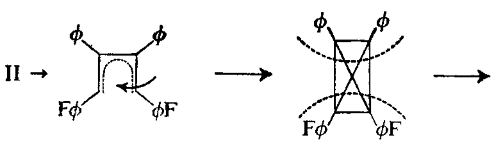
* Relative to the integrated intensity of the metastable at 81·0.

dependence or significant ionizing-voltage dependence[7] of the ratio for all of these tetracyclones demands that if a mixture is present, it is a mixture of ions of nearly identical stability or that the rate of interconversion between the forms is not strongly dependent on the internal energy of the ion. This behavior seems different from previously reported cases,[7,8] and interpretation of the data in terms of a single structure was deemed worth discussion.

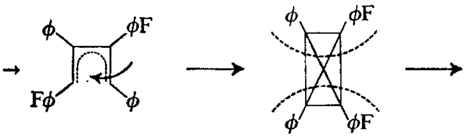
It will be appreciated that there is no significant variance in the intensity ratio of the peaks at *m/e* 178 and 214 in all three compounds (see Tables 1 and 3) or in the ratio of the integrated intensities of the metastables connecting these peaks to the $[M - CO]^{+\cdot}$ ion (see Tables 2 and 3). This indicates that the difluorinated and unfluorinated portions of the $[M - CO]^{+\cdot}$ ion always have the same symmetrical relationship with respect to each other. The invariance also suggests that the small deviation of the ratio from unity is caused by the small substituent effect of the fluorine, which induces only a slight alteration in bond lengths and strengths in the central four-carbon structure. It is a fair approximation to argue, then, that there is some symmetry element in the structure which converts these two portions into each other. The distortion from a regular tetrahedron cannot destroy this element; it does, however, disturb the formation of the monofluorinated fragment, which in I and II is less than it should be and in III is greater. A consistent symmetry is D_{2d}. A possible scheme which superficially fits this interpretation and explains the difference in the amount of $C_{14}H_9F^{+\cdot}$ formed from I and II, on the one hand, and III on the other may be described with reference to eqns. 4 to 6. Let the ions twist as the



excessive formation of $C_{14}H_8F_2^{+\cdot}$ and $C_{14}H_{10}^{+\cdot}$ (4)



excessive formation of $C_{14}H_8F_2^{+\cdot}$ and $C_{14}H_{10}^{+\cdot}$ (5)

III →


excessive formation of $C_{14}H_9F^{+}$ (6)

CO molecule is lost, with simultaneous stretching of the former 2,3 and 4,5 bonds. Let the ions close to the first available distorted tetrahedral structure after the 2,3 bond has begun to pass over the 4,5 bond. Then the disintegration of this tetrahedron, which has D_{2d} symmetry if the fluorines are neglected, will produce more of the 'diphenylacetylenes' with the 3,4 bond intact and with the 2,5 bond intact, because the other bonds, being longer, are more easily broken. In this fashion I and II will produce somewhat less than the anticipated amount of $C_{14}H_9F^{+}$ (ratio 1:<4:1) and III will produce more (ratio 1:>4:1).

While this argument leads to the correct distributions, it needs to have some aspects counter to intuition explained away. First, the stretching of the former 2,3 and 4,5 bonds is hard to explain without invoking promotion of an electron in the pi system. If this system resembles that of butadiene, removal of an electron from the highest filled Hückel orbital would lower the electron density in the bonds which have to stretch to fit the model; simple promotion of an electron from this orbital to the lowest unoccupied Hückel molecular orbital (with the site of the charge at some other non-interacting site, presumably) should produce contraction of the 3,4 bond in addition to extension of the 2,3 and 4,5 bonds. It is also unreasonable to expect the molecule to twist only to the first D_{2d} structure, and then to stop rotating and fragment unless the barrier to rotation is so high that fragmentation completes very efficiently with isomerization. A documented example of such competition is the case of the ligands of 1,1′-divinylferrocene, some of which can expand to cycloheptatrienyl before they lose C_2H_2.[8] Finally, a case must be made for the reason for distortion of the tetrahedron from T_d symmetry: at least a crude calculation suggests that the ground state of the tetrahedrane ion is degenerate, so that Jahn-Teller distortion would be expected.

In a series of elegant communications, Williams and his co-workers have used specific deuterium labeling to study the scrambling of ring positions in heterocycles on electron impact,[9,10] while Jennings has observed scrambling of ring positions in labeled benzenes on electron impact.[11] Both have suggested a parallelism between the photochemical and mass-spectral behavior of these compounds, invoking valence tautomers to explain the scrambling. Hoffmann and Woodward have predicted that there is a photochemical interconversion to be expected between cyclobutadiene, tetrahedrane, and two molecules of acetylene, on the basis of conservation of orbital symmetry.[12] It is amusing to contemplate our results in terms of a photochemical analogy, therefore, and to hypothesize that if sufficient cyclobutadiene can ever be accumulated for a photochemical study, this mass-spectral study suggests that it may proceed through a tetrahedral structure to photoproducts.

EXPERIMENTAL

The mass spectra were recorded on a Hitachi RMU-6E mass spectrometer with the source at 160° and probe temperatures from ambient to over 300° to check for pyrolysis. The ionizing current was 80 μA and the electron energy for normal scans 75 eV; low-voltage scans at (nominal) 20 eV and 15 eV were also recorded. Column chromatography was carried out with Merck reagent aluminum oxide 'Suitable for Chromatographic Adsorption,' and elemental analyses were done by Galbraith Laboratories, Knoxville, Tennessee.

Pyrolysis[13,14] of the calcium salt of *p*-fluorophenylacetic acid (Aldrich) gave 1,3-*bis*(*p-fluorophenyl*)*propanone*-2 in 63% yield after treatment with decolorizing carbon. The analytical sample was recrystallized from ethanol and had m.p. 65 to 65·5° (Found: C, 73·40; H, 4·90. $C_{15}H_{12}F_2O$ requires C, 73·15; H, 4·91).

This ketone and benzil were condensed by Fieser's method[15] to give 2,5-*bis*(*p-fluorophenyl*)-3,4-*diphenylcyclopentadienone* (II) in 73% yield after recrystallization from benzene-ethanol. The analytical sample had m.p. 203 to 204° (Found: C, 83·07; H, 4·27. $C_{29}H_{18}F_2O$ requires C, 82·83; H, 4·31).

The preparation of III was initiated by the condensation of *p*-fluorobenzaldehyde (Aldrich) and acetophenone in BF_3/acetic acid[16] to yield 4-fluorochalcone, m.p. 87 to 88·5°, reported m.p. 87°.[16] The chalcone (12·7 g, 0·056 mole) and 4′-fluoro-2-phenylacetophenone (Aldrich 4′-fluorodeoxybenzoin, 12·7 g, 0·059 mole) were dissolved in 40 ml. C_2H_5OH and 5 ml. 1 N $NaOC_2H_5$ was added. After 30 minutes the precipitate was collected and crystallized from isopropyl alcohol to give 20 g (81%) of crude 1,3-*bis*(*p-fluorophenyl*)-2,5-*diphenylpentane*-1,5-*dione* (IV), the Michael product; the procedure is analogous to those of Knoevenagel[17] and Dilthey.[18] Four recrystallizations were necessary to reach a constant m.p., 162 to 167·5° (Found: C, 79·34; H, 4·80. $C_{29}H_{22}F_2O_2$ requires C, 79·08; H, 5·03).

The dione (IV) was reduced to the cyclopentanediol with Zn in acetic acid and the diol dehydrated without isolation to 2,4-*bis*(*p-fluorophenyl*)-3,5-*diphenylcyclopentadiene* (V) in warm isobutyl alcohol saturated with HCl, by use of the general procedure of Mehr, Becker and Spoerri.[19] After recrystallization from benzene-ethanol three times (51% yield), the diene had m.p. 169 to 172·5° (Found: C, 85·81; H, 4·92. $C_{29}H_{20}F_2$ requires C, 85·69; H, 4·95).

The cyclopentadiene was oxidized to 2,4-*bis*(*p-fluorophenyl*)-3,5-*diphenylcyclopentadienone* (III) with *p*-dimethylaminonitrosobenzene by means of the generalized procedure[19] in 87% yield. The analytical sample was recrystallized twice from benzene-ethanol, m.p. 202 to 203° (Found: C, 82·96; H, 4·22. $C_{29}H_{18}F_2O$ requires C, 82·83; H, 4·31).

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