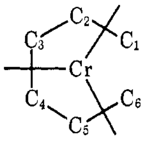
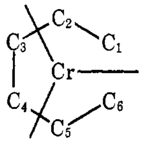
most probably rotated through 60°, the CrC≡O axes then bisecting the C_2–C_3, C_4–C_5 bonds, and the C_1–C_6 distance (b). In solution, rapid rotation of the $Cr(CO)_3$ group seems possible,[29] but since the species a and b are certainly of different energy, only one will predominantly influence the chemical shifts in this case. The X-ray data suggest that the low-energy conformers are of type a for II and type b for I. This prevents an averaging out of the specific shielding effect associated with each conformer.



a



b

The above argument is supported by results published on the nmr spectra of chromium tricarbonyl complexes of naphthalenes, where the relative resonance position of the protons[30] and the orientation of the $Cr(CO)_3$ group[31] parallel the situation met with II. Model calculations[4] based on assumed anisotropies seem at present not justified, since nothing is known about the nature of the observed shielding. The upfield shift of the proton resonances due to the complexation in aromatic compounds, such as III, is evidently not caused mainly by a reduction of the ring current effect, as suggested by Fritz, *et al.*,[30] since the shielding effects found for complexes with olefinic ligands, such as I and IV, are of the same order of magnitude.

The over-all upfield shift obtained for the bridge protons in II, as compared to those of III (Table II), seems best explained by a long-range shielding effect of the $Cr(CO)_3$ group, which might also be responsible for the change of the resonance frequencies in the uncoordinated half-ring.

The possibility of an intramolecular exchange of the chromium tricarbonyl group between the two half-rings of II was tested. Thermal instability of the compound, however, prevented the observation of spectra at elevated temperatures (>+100°).

Experimental Section

Analytically pure samples of I and II, respectively, were transferred to 5 mm o.d. Pyrex tubes equipped with ground joints. The tubes were evacuated on the vacuum line and dry, pure benzene-d_6 was distilled into the tube to give *ca.* 1 *M* solutions. Tetramethylsilane (*ca.* 5% by volume) was added and the tubes were sealed under vacuum after degassing the solutions.

Spectra were recorded with a Varian A60-A nmr spectrometer equipped with a Hewlett-Packard audiooscillator Model 202 A and a Hewlett-Packard electronic counter Model 5212 A using standard side-band technique. Experimental line positions were determined by interpolation and averaging over ten spectra obtained in the two directions of the magnetic field. When completely resolved, the probable error was in the order of 0.05 Hz. Decoupling experiments were performed with a Varian HA-100 nmr spectrometer using frequency sweep mode and a Hewlett Packard audiooscillator Model 4204 A.

Acknowledgment. We are indebted to Professor E. Vogel for support of this work and to Diplom-Chemiker B. Haas for a sample of I. Computations were performed at the Institut für Instrumentelle Mathematik, Bonn, using an IBM 7090 computer. Support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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(29) D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *Chem. Commun.*, 231 (1966).

(30) B. Deubzer, H. P. Fritz, C. G. Kreiter, and K. Öfele, *J. Organometal. Chem.* (Amsterdam), 7, 289 (1967).

(31) V. Kunz and W. Nowacki, *Helv. Chim. Acta*, **50**, 1052 (1967).

Tetrahedral Structures of Unexpected Stability. On Distinguishing Randomization Mechanisms in the Mass Spectral Fragmentation of Substituted Cyclopentadienols

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Contribution from the Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina 27514. Received October 3, 1968

Abstract: Pentaphenylcyclopentadienol molecular ions show partial hydrogen scrambling, as well as partial phenyl scrambling, before they fragment in the mass spectrometer. A major route for decomposition is the stepwise loss of the elements of aryl and CHO, to give a labeled $C_4Ph_4\cdot^+$. Labeling experiments suggest a tetrahedral symmetry for this species at some point before its further decomposition. The *p*-fluoro-labeling experiments suggest that the phenyl carbon skeleton remains intact, while deuterium labeling shows scrambling of hydrogens on the skeleton. The observation of this species after so unlikely a mode of formation, coupled with previous observations, offers the possibility that the tetraphenyltetrahedrane radical cation may possess unusual stability in mass spectral decompositions, like the tropylium ion in other systems.

The classic epitome of labeling experiments in mass spectrometry is the discovery of the symmetrical tropylium structure for $C_7H_7^+$.[1] Its observation in the spectrum of ethylbenzene was followed by studies of other aromatic systems and cycloheptatriene which showed the same result.[2] The spectra of many isomers of $C_7H_8\cdot^+$ have so many features in common with those of the spectrum of toluene that the tropylium structure has been postulated for the $C_7H_7^+$ ion in the

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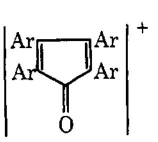
(1) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

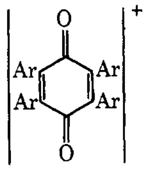
(2) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

spectra of compounds as diverse as norbornadiene[3] and 1-ethynylcyclopentene.[4,5] While some substituent-effect studies[6–8] indicate that the symmetrical tropylium structure is not universally formed, so many cases have been given reasonable documentation that it is of general interest to find a derivative of $C_7H_7^+$ which appears not to be a tropylium ion. Such far-ranging uncovering of this structure would suggest that its energetics of formation are particularly favorable, and in fact the symmetrical structure seems to be the most stable even when the C_7H_7 species acts as a ligand, if one accepts the simplest possible explanation of some ferrocene spectra.[9]

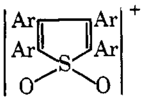
As an outgrowth of work on substituent effects in mass spectra,[10] we have recently proposed an additional kind of labeling technique; instead of replacing protium by deuterium, one may replace phenyl by *p*-fluorophenyl.[11] This substitution takes advantage of the small effect on ion intensities[10a,b] when the *para* hydrogen of an inert (or at least a ground-state) phenyl ring is replaced by fluorine. At least two examples of H–D labeling are generally paralleled by C_6H_5–FC_6H_4 labeling results in unsaturated systems: scrambling of substituents occurs before fragmentation of the molecular ion in thiophenes, but is much reduced in furans.[12] Such observations may eventually be of such a broad scope that the chemistry of the decompositions may be viewed entirely in terms of the central carbon or hetero system instead of its interaction with phenyl substituents.



$\xrightarrow{-CO}$ $C_4Ar_4^+$ (1)

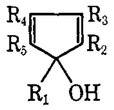


$\xrightarrow{-2CO}$ $C_4Ar_4^+$ (2)



$\xrightarrow{-SO_2}$ $C_4Ar_4^+$ (3)

This new substitution method has been applied to several systems which give an ion corresponding to $C_4(C_6H_5)_4\cdot^+$ by the fragmentation of the molecular ion of the unsubstituted compound. In the decomposition of tetracyclones (eq 1),[13] tetraarylquinones (eq 2),[14] and tetraphenylthiophene dioxides (eq 3),[15] the scrambling of labels before further decomposition of the $C_4Ar_4\cdot^+$ ions indicated that these species possessed a tetrahedral symmetry at some time. No especial driving force could be attributed to the mode of formation of such an ion from the ketonic precursors; the loss of CO from aliphatic cyclic ketones is not common, though not unknown.[16] The fact that quinones and cyclopentadienones characteristically lose CO may give a hint of the stability of the ionic product. Similarly, the loss of SO_2 from the molecular ions of cyclic sulfones is not uncommon;[17] other pathways clearly indicating rearrangements are also well known. We have engaged in a study of the generality of the formation of $C_4Ar_4\cdot^+$ from uncommon sources, in order to ascertain whether this ion has sufficient stability to divert fragmentation from other routes. Here are the details of decomposition of derivatives of 1,2,3,4,5-pentaphenylcyclopentadien-2,4-ol-1 (Ia).



Ia, $R_1 = R_2 = R_3 = R_4 = R_5 = C_6H_5$
b, $R_1 = FC_6H_4$; $R_2 = R_3 = R_4 = R_5 = C_6H_5$
c, $R_1 = R_2 = R_5 = FC_6H_4$; $R_3 = R_4 = C_6H_5$
d, $R_1 = R_2 = R_4 = FC_6H_4$; $R_3 = R_5 = C_6H_5$

The mass spectrum of the parent compound is given in Table I. It is of interest that at least a fraction of the

Table I. Mass Spectrum of 1,2,3,4,5-Pentaphenylcyclopenta-2,4-dien-ol-1[a]

m/e	Rel inten	*m/e*	Rel inten
77	9	279	8
105	12	280	4
139	3	289	4
152	3	307	3
165	7	339	2
167	6	341	2
176	3	355	2
177	2	356	8
178	25	357	8
179	7	358	2
202	3	367	2
252	4	384	5
265	6	385	9
267	6	386	5
277	4	462	100
278	4	463	38
		464	7

[a] All peaks above 2% relative intensity are reported. There are in addition prominent metastables at 56.5 [$C_6H_5CO^+$, 105 → $C_6H_5^+$, 77], 89.0 [$(C_6H_5)_4C_4\cdot^+$, 356 → $C_{14}H_{10}\cdot^+$, 178], 218.7 [356 → $(C_6H_5)_3C_4^+$, 279], 320.8 [$M^{+}\cdot$, 462 → $(C_6H_5)_4C_5HO^+$, 385], and 329 [385 → 356].

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(3) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

(4) V. Hanuš, *Nature*, **184**, 1796 (1959).

(5) For reviews, see: (a) S. Meyerson, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **26**, 257 (1965); (b) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453; (c) M. M. Bursey and F. W. McLafferty, "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, John Wiley & Sons, Inc., New York, N. Y., 1968, p 257.

(6) J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Am. Chem. Soc.*, **84**, 4 (1962); F. Meyer and A. G. Harrison, *Can. J. Chem.*, **42**, 1762 (1964).

(7) P. Brown, *J. Am. Chem. Soc.*, **90**, 2694 (1968).

(8) F. W. McLafferty and M. M. Bursey, *ibid.*, **90**, 5299 (1968).

(9) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *ibid.*, **90**, 973 (1968).

(10) See particularly: (a) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 529 (1966); (b) M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967); M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

(11) M. M. Bursey, R. D. Rieke, T. A. Elwood, and L. R. Dusold, *J. Am. Chem. Soc.*, **90**, 1557 (1968).

(12) T. A. Elwood, P. F. Rogerson, and M. M. Bursey, *J. Org. Chem.*, **34**, 1138 (1969). *Cf.* D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Letters*, 1777 (1968).

(13) M. M. Bursey and T. A. Elwood, *Org. Mass Spectrom.*, **1**, 531 (1968).

(14) T. A. Elwood and M. M. Bursey, *ibid.*, **1**, 537 (1968).

(15) M. M. Bursey, T. A. Elwood, and P. F. Rogerson, *Tetrahedron*, **25**, 605 (1969).

(16) See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 143.

(17) D. S. Weinberg, C. Stafford, and M. W. Scoggins, *Tetrahedron*, **24**, 5409 (1968).

ion yield of m/e 356 is produced by the loss of CHO from the precursor at m/e 385, and although the region where a metastable for the simultaneous loss of both radicals would be expected is obscured by intense normal peaks and other metastables relating these by hydrogen losses, in the *p*-fluoro derivatives Ib, Ic, and Id there are very weak metastables corresponding to the analogous processes.[18] Now the formation of an odd-electron species (m/e 356) from an even-electron species (m/e 385) is an atypical process, since it requires formation of two radical species from an ion in which all electrons are potentially paired.[19] There are not many examples of such processes in the literature; in those cases which have been found, there is some particular stability associated with the product—creation of a larger conjugated system is a driving force.[20] In general, these reactions have not been studied with the purpose of generalization of the conditions under which they occur.

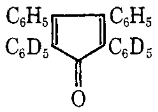
If indeed the C_6H_5 and CHO moieties are lost as a single molecule, this process might also point to especial stability of the $C_4(C_6H_5)_4\cdot^{+}$ ion. The loss of benzaldehyde, a stable molecule, could also provide a driving force, but to our knowledge there are no parallels to this loss of the alcohol function as an aldehyde molecule. Whatever the origin of this fragment, then, it could reflect some special stability. Presuming that the structure of $C_4(C_6H_5)_4\cdot^{+}$ might be similar to its structure when it is formed by the loss of CO or SO_2 from a precursor, we investigated it with the *p*-fluoro-labeling technique, using the label distribution in the metastable peaks corresponding to the metastable for 356 → 178 in the parent compound.

The spectra of the three derivatives quite unexpectedly gave evidence of label scrambling in the molecular ion. Table II lists the ratios of phenyl to *p*-fluorophenyl labels found for loss of C_6H_5 + CHO, and also in the benzoyl ion intensities. The approach to complete scrambling before the production of both kinds of ions is variable, but in general the intensities of the $C_4Ar_4{}^{+}$ are close to those predicted for complete scrambling (and also for $\log (Z/Z_0) = 0$, an assumption which is a rough enough approximation to make quantitative interpretation of differences between theory and experiment difficult[11,13]). Equilibration appears to be less complete before $ArCO^{+}$ is formed. The lack of immediate achievement of symmetry for the precursors of $ArCO^{+}$ would indicate, for these ions at least, randomization does not proceed through a single structure of (local) C_{5v} symmetry, but is achieved by stepwise processes.

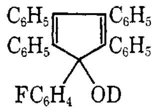
Table II. Selected Ion Intensity Ratios in the Spectra of Ib, Ic, and Id

Compound	Found [M − 106] [M − 124]	Found [105] [123]	Calcd for scrambling 0%	100%
Ib	73:27	59:41	0:100	80:20
Ic	42:58	30:70	0:100	40:60
Id	41:59	34:66	0:100	40:60

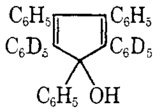
This troublesome scrambling suggested that a deeper study of the structure was necessary to determine whether the different positions on the phenyl rings themselves were subject to exchange. We found, first of all, that in 2,5-bis(pentadeuteriophenyl)-3,4-diphenylcyclopentadienone (tetracyclone-d_{10}, II), the fragmentation of the $(M - CO)\cdot^{+}$ ion occurs with scrambling of the rings, but not scrambling of hydrogens between rings. This conclusion was based on inspection of the $C_{14}H_{10}\cdot^{+}$ ions and their metastable precursors of the formula $C_{28}H_{20}\cdot^{+}$, or $(M - CO)\cdot^{+}$. The $C_{14}H_{10}\cdot^{+}$ ions appeared at m/e 178 $(C_{14}H_{10})\cdot^{+}$, 183 $(C_{14}H_5D_5)\cdot^{+}$, and 188 $(C_{14}D_{10})\cdot^{+}$ almost exclusively; for example, the d_1 ion had <1% of the intensity of the d_0, and the d_4 and d_6 ions had <3% of the intensity of the d_5. The intensities of the other possible ions were similarly very low. The metastable precursors appeared at 86.8 (calcd for 366 → 178, 86.6), 91.7 (calcd for 366 → 183, 91.6), and 96.6 (calcd for 366 → 188, 96.6), in an intensity ratio of 1:3.8:1.03. Intensities of normal daughters suggested a possible competing contribution to $[C_{14}H_5D_5\cdot^{+}]$ from other precursors, similar to previous examples.[14–15] This once again suggests a tetrahedral structure (V) for this ion, in harmony with previous results.[13] For a perfect tetrahedron, a ratio of 1:4:1, just outside reproducibility limits for measurement, would be expected. The lack of scrambling of hydrogens between rings is also consistent with the *p*-fluoro-labeling results: the *p*-fluoro substituent exhibits ground-state behavior expected for retention of positional identity in this system.[11] Evidently, then, for the original system, processes leading to hydrogen scrambling do not compete effectively with dissociation of the metastable $C_4Ar_4\cdot^{+}$, and the tetraphenyltetrahedrane structure is a fair model for the structure through which such ions pass before dissociation. This result stands in opposition to many fragmentation processes involving phenylated compounds where C_6H_5 is lost after intramolecular hydrogen scrambling.[21]



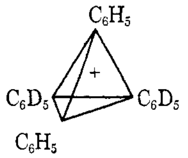
II



III



IV



V

Though this first case showed no scrambling, the cyclopentadienols decompose by a much less straightforward route, which could conceivably be complicated by hydrogen scrambling; the first step does involve a loss of C_6H_5 and therefore is similar to the literature cases[21] where scrambling was noted. In the spectrum of the deuterated alcohol III, we found that the first loss, that of C_6H_5 or FC_6H_4, does occur after partial

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(18) These metastable peaks may merely indicate a rapid sequential loss of the C_6H_5 and CHO fragments, rather than their simultaneous loss as C_6H_5CHO; *cf.* K. R. Jennings, *Chem. Commun.*, 283 (1966).

(19) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, p 99.

(20) Several examples, with varying degrees of support for the structures postulated, are given by P. Longevialle, *Bull. Soc. Chim. France*, 437 (1966).

(21) *E.g.*, *cf.* S. Meyerson, H. Hart, and L. C. Leitch, *J. Am. Chem. Soc.*, **90**, 3419 (1968).

hydrogen scrambling, assuming nondecomposing and decomposing molecular ions to come from identically wall-equilibrated alcohol molecules. Likewise, the loss of C_6H_6 or FC_6H_5 occurs after scrambling. Deuterium is incorporated into C_6H_5 to the extent of 20%, and into C_6H_6 to the extent of 45%; the figures for the losses of the fluorine-containing species are comparable. Because of exchange problems, interpretation here must be very cautious.

With this initial complication, it was not surprising to find heavy scrambling in the pentaphenylcyclopentadienol IV. So much scrambling has occurred before $C_4Ar_4\cdot^+$ fragments in this case that the daughters ($C_{14}H_{10}\cdot^+$) of $C_4Ar_4\cdot^+$ are scattered at all the masses between that of the d_0 and that of the d_{10} compound.[22] It was impossible to assign meaningful values to the contributions of each ion, with the contributions of other fragments from other pathways complicating the spectrum with unknown amounts of scrambled ions. As an indication of the scrambling in $C_4Ar_4\cdot^+$ itself, metastable $C_4Ar_4\cdot^+$ was no longer found at the three distinct positions found for it in the spectrum of II, but instead appeared as a very broad metastable centered at about *m/e* 92. So many daughters were now formed that overlapping metastable peaks removed the troughs between those found in the spectrum of II.

This entirely different behavior with respect to hydrogen scrambling in II and IV made it of great interest to study the fluorine-labeling patterns of decomposition of metastable $C_4Ar_4\cdot^+$, to determine whether the carbon skeleton of this ion was affected enough to influence the substituent effect of *p*-F during hydrogen scrambling.

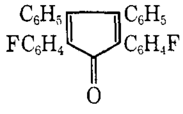
Because of the production of interfering metastables representing the possible decompositions of $C_4Ar_4\ ^+$, this randomization of the molecular ion dictated the choice of compounds for study of $C_4Ar_4\ ^+$: Ic and Id have three fluorophenyl groups, but at first sight two fluorophenyl groups could have served just as well. The metastable $C_4(C_6H_5)_2(FC_6H_4)_2\ ^+$ ions, however, were expected to appear at *m/e* 80.8 (392 → 178), 98.0 (392 → 196), and 116.8 (392 → 214). In addition to this disubstituted $C_4Ar_4\ ^+$, the trisubstituted molecular ion must also give some trisubstituted $C_4Ar_4\ ^+$, which would decompose to give metastables at *m/e* 93.7 (410 → 196) for the route to monosubstituted $C_2Ar_2\ ^+$, and 111.7 (410 → 214) for disubstituted. On the other hand, a disubstituted molecular ion would produce both disubstituted and monosubstituted $C_4Ar_4\ ^+$, which would decompose to give metastables at *m/e* 84.7 (374 → 178) for the unsubstituted $C_2Ar_2\ ^+$ and 102.7 (374 → 196) for the monosubstituted. These latter two metastables are more apt to interfere with those from the desired ion, and so the trisubstituted compounds were used for the study.

Results of intensity measurements for the metastable peaks at *m/e* 80.8, 98.0, and 116.8 in the spectra of Ic and Id are given in Table III, along with the corresponding intensity measurements from compounds VI and VII.[13] The similarity of the data for the alcohols to those for the model tetracyclones is striking. The relative populations following the different decomposition pathways to monosubstituted, disubstituted, and unsubstituted products are the same for both sets of compounds.

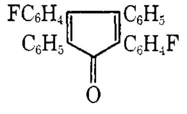
Table III. Relative Intensities of Metastable $C_4Ar_4\ ^+$ Ions in the Mass Spectra of Ic, Id, VI, and VII[a]

	m/e 80.8	*m/e* 98.0	*m/e* 116.8
Ic	1	3.4	0.88
VI	1	3.2	0.93
Id	1	5.2	0.92
VII	1	5.2	0.87

[a] Intensities relative to the intensity of the metastable at *m/e* 80.8 in each spectrum, corrected to a linear *m/e* scale by a factor determined by measuring the actual scale contraction in each spectrum.



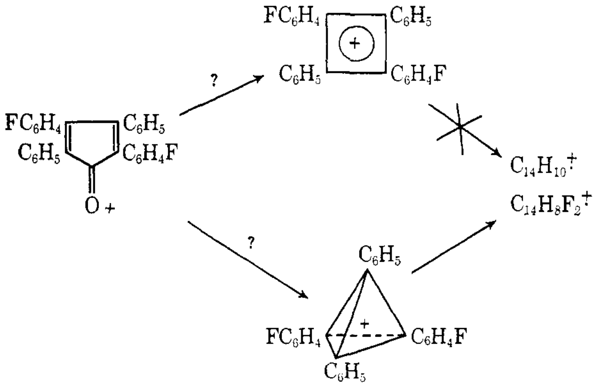
VI



VII

This indication of scrambling is not to be expected if there is carbon-skeleton reorganization within the phenyl rings before fragmentation of the $C_4Ar_4\cdot^+$ ion. In such a case, the substituent effect of the fluorine would most likely be significantly altered from the model system; examples of deviations from expected behavior have been collected[11] and show variance from the small substituent effect noted here by almost an order of magnitude in either direction. Transmission of the same substituent effect for fluorine found in ground-state chemistry argues for a relatively undisturbed π system connecting it and the reaction site. Apparently this may be reconciled with the heavy scrambling for hydrogen in this system by an argument invoking rapid exchange of hydrogens on a nonrearranging carbon skeleton.

If the data for the cyclopentadienols and their models, the tetracyclones, suggest identity of decomposition routes with respect at least to the carbon skeleton, then further interpretation is similar. As we have argued before, the formation of $C_{14}H_8F_2\cdot^+$ (*m/e* 214, metastable at 116.8) from the (M − CO)$\cdot^+$ ion of VII militates against merely an unreorganized planar structure for metastable $C_4Ar_4\ ^+$ ions, for a bond approximately equal in strength to that between the two carbons bearing the unsubstituted phenyl rings must have formed prior to fragmentation of the ion (eq 4).[13] To repeat a further point, if the data are interpreted in terms of a single structure, then that structure must be a tetrahedron of less than T_d symmetry. The distribution of intensities for T_d symmetry would be $C_{14}H_{10}$:$C_{14}H_9F$:$C_{14}H_8F_2$ (metastables at *m/e* 80.8, 98.0, 116.8) = 1:4:1, or, after correction by a reason



(4)

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[22] The peak at *m/e* 183 ($C_{14}H_5D_5\cdot^+$) is much larger than the rest. It probably results from the formation of "diphenylacetylene" ion directly from the molecular ion, without any scrambling.

able substituent effect based on the reflection of the intensity at *m/e* 116.8 of this point alone, 1:3.8:0.90. The intensities of the monosubstituted-product metastable peaks in each set of compounds vary from 3.2 to 5.2, bracketing the expected value, while those for the other products retain a constant value throughout all series. This has been interpreted as indicating a D_{2d} symmetry for the tetrahedral structure.[13]

The question arises of the validity of the assumption of a single structure. The preceding discussion of metastable intensities reflects only the energetics of ions with a relatively narrow energy range, consisting of species only very slightly above the activation energy for the dissociation into $C_2Ar_2\cdot^+$ and C_2Ar_2. As far as these species are concerned, the $C_4Ar_4\cdot^+$ from all four sources—tetracyclone, quinone, sulfone, and now cyclopentadienol—is identical. The potential energy surface for this species, whatever it is, could include various linear and planar closed forms as well as the tetrahedral structure; the D_{2d} structure might well be a very low energy pass (sufficiently low that metastable ions could attain it) between other structures which seem intuitively more stable.

On the other hand, the wide-range energetics of the rapidly decomposing ions (the normal mass spectrum) can contribute some information to this point. A more intense normal $C_{14}H_5D_5\cdot^+$ peak than expected indicates that the $C_2Ar_2\cdot^+$ ions come from a number of sources, including at least $C_4Ar_4\cdot^+$ and probably the molecular ion, in the cyclopentadienols. In one previously reported case, the tetracyclone precursor,[11] the $C_2Ar_2\cdot^+$ seems to be formed from only one precursor, $C_4Ar_4\cdot^+$; the intensity ratio of the unfluorinated, monofluorinated, and difluorinated normal peaks is essentially independent of ionizing voltage down to values very near the appearance potentials. The intensity ratio of these normal peaks is again different from the theoretical 1:4:1 in this case;[11,13] thus a single type not subject to total equilibration might be suggested for these normal ions. In each of the other precursors, the spectra might be explained by a superposition of other sources of $C_2Ar_2\cdot^+$ on the distribution from this structure. Alternatively, this observation in the tetracyclones may merely indicate that the D_{2d} form is an especially low energy pass between other structures, and that other forms which would totally equilibrate the various ring positions are of unexpectedly high energy.

The consistency of the *p*-fluoro-labeling results with previous data, in spite of the hydrogen scrambling observed for the cyclopentadienols alone, raises a number of questions about substituent effects in general in the $C_4Ar_4\cdot^+$ system. We are pursuing other unusual sources of this ion and attempting to generate the planar structure free of tetrahedral contaminant.[22a]

Experimental Section

General. Mass spectra were recorded on a Hitachi RMU-6E instrument at 75 eV, with an ionizing current of 80 μA; samples were introduced on the direct probe at temperatures between 180 and 200°. Chromatographic purifications were performed on Merck aluminum oxide "Suitable for Chromatographic Adsorption," the desired products being eluted with benzene and preceded by small amounts of a biphenyl impurity (?) and tetracyclone in petroleum ether (bp 90–115°)–benzene fractions. Melting points were determined on a Thomas-Kofler apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Pentaphenylcyclopentadienol was prepared by the addition of tetracyclone to an ethereal solution of excess phenylmagnesium bromide, according to the procedure of Ziegler and Schnell.[23]

1-*p*-Fluorophenyl-2,3,4,5-tetraphenylcyclopentadien-2,4-ol-1 (Ib) was prepared in similar fashion from tetracyclone and the Grignard reagent from *p*-bromofluorobenzene (Aldrich Chemical Co., Inc.). After chromatography and recrystallization from petroleum ether and then acetic acid, it had mp 180–182°.

Anal. Calcd for $C_{35}H_{25}OF$: C, 87.47; H, 5.24. Found: C, 87.82; H, 5.03.

3,4-Diphenyl-1,2,5-tris(*p*-fluorophenyl)cyclopentadien-2,4-ol-1 (Ic) was similarly prepared from 2,5-bis(*p*-fluorophenyl)-3,4-diphenylcyclopentadienone (VI)[13] and after recrystallization from petroleum ether and then acetic acid had mp 176–178°.

Anal. Calcd for $C_{35}H_{23}OF_3$: C, 80.77; H, 4.78. Found: C, 81.02; H, 4.51.

2,4-Diphenyl-1,3,5-tris(*p*-fluorophenyl)cyclopentadien-2,4-ol-1 (Id) was similarly prepared from 2,4-bis(*p*-fluorophenyl)-3,5-diphenylcyclopentadienone (VII)[13] and after recrystallization from petroleum ether and then acetic acid had mp 146–149°.

Anal. Calcd for $C_{35}H_{23}OF_3$: C, 80.77; H, 4.78. Found: C, 80.76; H, 4.75.

2,5-Bis(pentadeuteriophenyl)-3,4-diphenylcyclopentadienone (II) was prepared by a standard sequence of steps from toluene-d_8 (Diaprep, Inc., Atlanta). These included synthesis of the labeled benzyl bromide,[24] phenylacetic acid,[25] 1,3-diphenylpropanone-2,[26] and tetracyclone.[27] The tetracyclone prepared by this route was found to be 5% d_8, 24% d_9, 71% d_{10}. The spectral data reported are corrected for this distribution as well as that of naturally occurring ^{13}C.

1-*p*-Fluorophenyl-2,3,4,5-tetraphenylcyclopentadien-2,4-ol-1-O-*d* (III) was prepared by triple exchange of Ib in D_2O and previously dried (CaH_2) dioxane on a vacuum line. The mass spectrometer was equilibrated repeatedly with D_2O for over an hour before spectra were recorded. The data reported were taken from a spectrum of a sample containing 69% d_1, 31% d_0, and are corrected for this isotopic distribution as well as that of ^{13}C.

2,5-Bis(pentadeuteriophenyl)-1,3,4-triphenylcyclopentadien-2,4-ol-1 (IV) was prepared by the addition of II to excess ethereal phenylmagnesium bromide.[23] The isotopic distribution was unchanged from that of II.

Acknowledgments. We express our gratitude for support by the Advanced Research Projects Agency, through Contract SD-100 with the University of North Carolina Materials Research Center, and acknowledge helpful discussions with Mr. Peter F. Rogerson. A referee's comments suggested the deuterium-labeling experiments.

[22a] Note Added in Proof. Professor Edward R. Thornton informs us of ^{13}C labeling studies of the $C_4H_4\cdot^+$ ion by Dr. Anthony Wu in progress in his laboratory. Results from these experiments should show whether the maximum scrambling we have observed is a property of the C_4 unit itself or whether the large phenyl groups exert great influence, possibly steric, on the energy surface.

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