A Comment on the Generality of Mass Spectral Labeling Techniques. Scrambling of the *p*-Fluoro Label in Tetraphenylfuran and Tetraphenylthiophene

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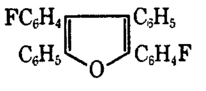
We report here on the scrambling, or lack of it, of the label in the mass spectral fragmentation of tetraphenylfuran and tetraphenylthiophene, using the *p*-fluoro labeling technique.[1] Studies have recently been published on hydrogen–deuterium scrambling in the spectra of furan and thiophene themselves.[2] Loss of positional identity was interpreted[2] in terms of the analogous photochemical behavior of substituted thiophenes,[3] and lack of such reactivity in substituted furans.[3,4] In view of the great number of hydrogen migrations known to exist in mass spectral decomposition patterns, and their lack of parallelism with migrations of heavier groups,[5] it would be appropriate to support or disprove the suggestion above—that the heavy atoms of the heterocyclic ring themselves lose positional identity, not just the attached hydrogens—by studies with a much heavier label. In addition, the hydrogen–deuterium scrambling was interpreted in terms of competitive rearrangement and fragmentation of the molecular ion; it would be valuable to know how these relative rates vary when the substituent is greatly modified.

Tetraphenylfuran (TPF), as expected for a large aromatic system, has an intense molecular ion accounting for almost half the total ion current; the other peaks of interest in its spectrum are at *m/e* 267 (loss of benzoyl), 165 (the common rearrangement product of polyphenylheterocycles[6] and other aryl systems[7,8]), 105, and 77. The unsymmetrically substituted compound I would be expected to show equivalent amounts of labeled and unlabeled products corresponding to each of these fragments even if there is no rearrangement in the molecular ion before fragmentation. The ratios of labeled to unlabeled peak intensities for the various fragments are given in column 3 of Table I. For the ions related to the molecular ion by a metastable peak, the intensities of the unlabeled and labeled fragments are sufficiently similar to confirm that fluorine acts as an essentially inert atom, as might be expected from its behavior in the formation of substituted[9] and unsubstituted[10] ions from *p*-fluorobenzophenone. We may then use these intensities as standard values for the interpretation of the spectrum of II, which would produce only *m/e* 123 ($FC_6H_4CO^+$) and 285 (loss of $FC_6H_4CO\cdot$) if there is no scrambling. As column 4 of Table I shows, this is very nearly the case; the intensities of these ions are more than an order of magnitude larger than the intensities of the corresponding unlabeled ions, which must arise by rearrangement of the molecular ion. A similar statement might be made for the ion of *m/e* 77 and its analog at 95, but there is no metastable connecting it with the molecular ion; its origin might well be decarbonylation of the benzoyl ion, for which a metastable ion is found. The ratios of the analogs of $C_{13}H_9^+$ do not change significantly.


I

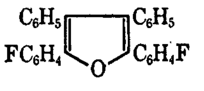
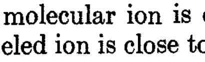

II

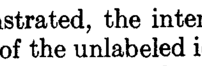
TABLE I

RATIOS OF LOSS TO RETENTION OF LABEL IN IONS IN THE SPECTRA OF LABELED TETRAPHENYLFURANS I AND II

Ion and intensity in TPF	Ions compared	Ratio in I	Ratio in II
77 ($C_6H_5^+$), 9%	95:77	0.6	7
105 ($C_6H_5CO^+$), 15%	123:105	0.8[a]	11[a]
165 ($C_{13}H_9^+$), 8%	201:183:165	1:6:0.3	1:6:0.3
267 (M − C_6H_5CO), 30%	285:303	0.9[a,b]	20[a,b]

[a] A metastable ion connecting each fragment to the molecular ion with similar peak intensity ratio as for the normal ions, is found. [b] The unlabeled peak is taken as *m/e* 303, the loss of unlabeled benzoyl.


III


IV

Likewise, tetraphenylthiophene (TPT) has an intense molecular ion that accounts for more than 70% of the total ion current. Fragment ions correspond to losses of H_2S (*m/e* 344), C_6H_6 (*m/e* 310), C_6H_6S (*m/e* 278), and C_6H_5CS (*m/e* 267), and to the formation of *m/e* 165, 121 ($C_6H_5CS^+$), and 77. For heavier ions, there are also peaks corresponding to the loss of one and two hydrogens accompying them as well. Again, the unsymmetrically substituted thiophene III may be used to examine whether equivalent amounts of labeled and unlabeled fragments are formed, as in column 3 of Table II. Again, for almost all cases in which relation to the molecular ion is demonstrated, the intensity of the labeled ion is close to that of the unlabeled ion, and consequently the *p*-fluoro substituent may be used in IV as an inert label. The spectrum of IV indicates that, unlike the spectrum of the furan II, considerable scrambling occurs in the thiophene. The scrambling is least, though still appreciable, in the formation of thiobenzoyl ions and loss of thiobenzoyl radicals, processes

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[6] J. H. Bowie, P. F. Donaghue, H. J. Rodda, and B. K. Simons, *Tetrahedron*, **24**, 3965 (1968).

[7] F. W. McLafferty, Advances in Chemistry Series, No. 40, American Chemical Society, Washington, D. C., 1963, p 64.

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[9] M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 1 (1967).

[10] M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 529 (1966).

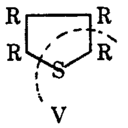
TABLE II

RATIOS OF LOSS TO RETENTION OF LABEL IN IONS IN THE SPECTRA OF LABELED TETRAPHENYLTHIOPHENES III AND IV

Ion and intensity in TPT	Ions compared	Ratio in III	Ratio in IV
77 ($C_6H_5^+$), 3%	95:77	0.6	2
121 ($C_6H_5CS^+$), 6%	139:121	0.9[a]	3[a]
165 ($C_{13}H_9^+$), 8%	201:183:165	*b*	*b*
267 (M − C_6H_5CS), 4%	285:303	1.0[c]	2.5[c]
278 (M − C_6H_6S), 4%	296:314	1.0[c,d]	1.1[c,d]
310 (M − C_6H_6), 6%	328–346	1.0[c,e]	1.7[c,e]

[a] Metastables of similar intensity ratio connect these to the molecular ion. [b] The peaks at 165 and 201 are buried in a rich doubly charged spectral region; the *m/e* 183 is at least a factor of 6 larger than either of these. [c] The ions formed by loss of the unsubstituted fragment (*m/e* 303, 314, 346) are taken as reference peaks. [d] The metastable for *m/e* 424 → 314 is present; the one for *m/e* 424 → 296 is buried in a doubly charged spectral region, and intensity comparisons cannot be made. [e] Both metastables (424 → 346, 328) are present but are distorted by other peaks.

which in the absence of experiments like these could have been formulated without formation of new bonds, as in V. The amount of scrambling is greater for the loss of the elements of benzene if this fragmentation is ascribed to direction by the heteroatom; here the process requires formation of a new C–H bond even at an elementary level of interpretation. Finally, the loss of C_6H_6S, a process requiring even more reorganization before fragmentation, shows almost complete equivalence of the different ring positions. All these observations fit a picture in which rearrangement is competitive with fragmentation, and in which obviously more complex pathways form products more slowly, so that a greater fraction of the products indicate a loss of positional identity. No comparison can be made with the loss of acetylene from thiophene,[2] since the analogous fragmentation does not occur in these compounds.



V

Our results extend those of Williams and support the photochemical analogy which he proposed.[2] On the one hand, the fact that heavy groups scramble like hydrogens in the thiophenes is accommodated by a process of formation of new bonds between C and S atoms of the ring, not simply hydrogen and aryl migrations about an intact thiophene nucleus. They support his concept of competitive rearrangement and fragmentation, particularly by contributing new kinds of fragmentations unavailable to the simple deuteriated molecules. Finally, they demonstrate the utility of the *p*-fluoro labeling technique as an adjunct in the determination of reaction mechanisms where some ambiguity possibly remains because of alternate interpretations of hydrogen–deuterium labeling results. The technique can also be applied to other systems, for example, quinones[11] and thiophene dioxides.[12] It does have limitations; it is impossible to use it to study scrambling in hexaphenylbenzene and pentaphenylpyridine, for example, because of the lack of sufficiently intense fragment ions in the spectra of these compounds.

Experimental Section

Mass spectra were recorded on a Hitachi RMU-6E instrument at 70 eV, with an ionizing current of 80 μA; the samples were introduced on the direct probe at temperatures between 60 and 100°. Melting points were determined on a Thomas–Kofler apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Samples of 2,4-bis(*p*-fluorophenyl)-3,5-diphenylthiophene (III) and 2,5-bis(*p*-fluorophenyl)-3,4-diphenylthiophene (IV) had been prepared in the course of another investigation.[12]

2,4-Bis(*p*-fluorophenyl)-3-diphenylfuran (I) was prepared from 2,4-bis(*p*-fluorophenyl)-3,5-diphenylcyclopentadienone[13] by singlet oxygen oxidation[14] to the substituted *cis*-dibenzoylstilbene, which was converted without isolation into the furan with Zn dust in refluxing acetic acid.[15] Chromatography on alumina and crystallization from ethanol gave product of mp 179–181°.

Anal. Calcd for $C_{28}H_{18}F_2O$: C, 82.33; H, 4.44. Found: C, 82.41; H, 4.43.

2,5-Bis(*p*-fluorophenyl)-3,4-diphenylfuran (II), mp 173–176°, was prepared analogously from 2,5-bis(*p*-fluorophenyl)-3,4-diphenylcyclopentadienone.[13]

Anal. Calcd for $C_{28}H_{18}F_2O$: C, 82.33; H, 4.44. Found: C, 82.41; H, 4.28.

Registry No.—I, 18741-99-6; II, 18749-93-4; III, 18742-00-2; IV, 18742-01-3.

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Internal Diels–Alder Additions of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes

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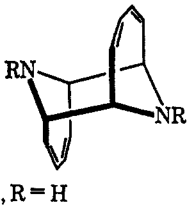
The syntheses of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**1a**) and its derivatives from 1-cyanoazepine were reported previously.[1] Attempts



1a, R = H
b, R = $CH_2CH{=}CH_2$
c, R = $CH_2CH_2CH{=}CH_2$

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