Tetrahedron Letters No.14, pp. 1777-1780, 1968. Pergamon Press. Printed in Great Britain.

STUDIES IN MASS SPECTROMETRY. PART XXVII(1). THE DECOMPOSITION OF FURAN, THIOPHEN AND DEUTERATED ANALOGUES UNDER ELECTRON IMPACT

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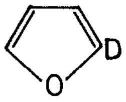
(Received in UK 10 December 1967)

The recent observations that H and D atoms in partly deuterated benzenes(2) and pyridines(3) can lose identity in metastable transitions in their mass spectra has prompted us to examine the behaviour of deuterated furans (I, II) and thiophens (III, IV, V) upon electron impact. The compounds I and III were prepared by treatment of the 2-lithio derivatives(4) with deuterium oxide, II was available by a literature procedure,(5) and IV and V by successive treatment of 2,5-diiodothiophen(6) and 2,3-dibromothiophen(7) with lithium butyl and deuterium oxide. All the compounds were isolated by preparative gas-liquid chromatography and the location of deuterium in I-IV established from proton magnetic resonance spectra.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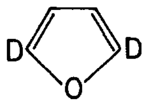
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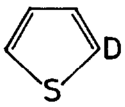
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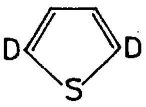
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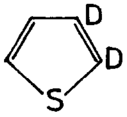
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The isotopic purities of the materials, as calculated from their mass spectra, are summarized in Table 1. Throughout this note, corrections for any possible primary isotopic effect have not been attempted because of the lack of reliable data.

TABLE 1

Isotopic Purities (%) of Labelled Furans (I, II) and Thiophens (III-V)

Compound	d_0	d_1	d_2	d_3
I	13	87	-	-
II	2	13.5	79	5.5
III	6	83	11	-
IV	-	4	95	1
V	7	22	71	-

Since the only abundant and clearly discernible "metastable peak" in the mass spectrum of furan is due to loss of carbon monoxide from the molecular ion, metastable transitions could not be used to evaluate possible H/D scrambling prior to, or accompanying fragmentation. Therefore, a spectrum of furan was obtained at a nominal 18ev, at which beam energy the mass region (m/e 38-44) containing abundant fragment ions exhibited only M - C_2H_2 (m/e 42), M - CO (m/e 40) and M - CHO (m/e 39) peaks (Table 2). The corresponding peak distributions from 2-d_1-furan (I) and 2,5-d_2-furan (II) are also given in the Table; the figures are corrected for ^{13}C isotope contributions and isotopic impurities, and also the total ion current is normalized to 100 units.

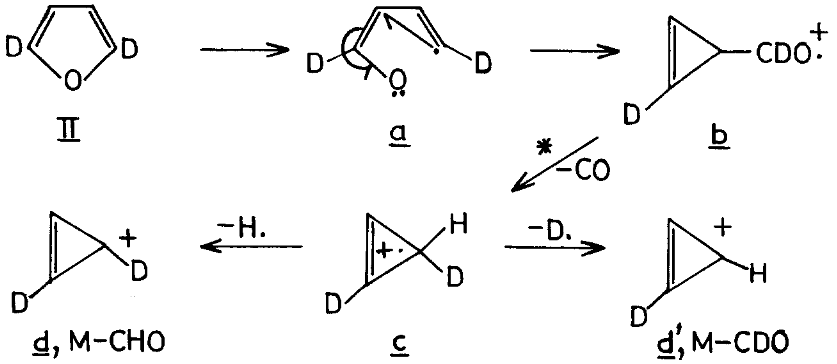
TABLE 2

Peak Distributions in the m/e 38-44 Regions of the 18ev Spectra of Furan, 2-d_1-Furan (I) and 2,5-d_2-Furan (II)

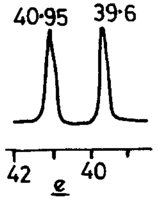
Compound	38	39	40	41	42	43	44 (m/e)
Furan	0	66 (M - CHO)	23 (M - CO)	0	11 (M - C_2H_2)	0	0
I	0	25 (M - CDO)	42 (M - CHO)	24 (M - CO)	5 (M - C_2HD)	4 (M - C_2H_2)	0
II	0.4	0.7	50.4 (M - CDO)	29.3 (M - CHO)	13.5 (M - CO)	5.4* (M - C_2HD)	0.25* (M - C_2H_2)

* In the case of 2,5-d_2-furan (II) only the figures marked with an asterisk have been corrected for the 5.5% of d_3-contaminant. The m/e 44 peak from II has also been corrected for the contribution from CO_2.

Although in the spectrum of II there is an apparent fall in the ion current carried by the M - CO and M - C_2H_2 type ions of furan itself (relative to M - CHO), the results indicate that hydrogen scrambling in furan prior to acetylene elimination occurs only to the extent of about 18% (complete H/D randomization in II would produce M - C_2D_2, M - C_2HD and M - C_2H_2 peaks in the ratio 1:4:1, while no scrambling would lead only to a M - C_2HD peak).(8) Unfortunately, the low intensity of the M - C_2H_2 ion from II calculated even on the basis of complete randomization, renders our results compatible with either (a) no randomization or (b) a maximum of 35% randomization, but complete equivalence of the hydrogens of furan prior to acetylene expulsion is excluded. In addition, hydrogen scrambling does not precede CHO^+ (m/e 29) formation from furan, since the spectrum of I contains CHO^+ and CDO^+ ions of approximately equal abundance (1.0:1.1), whereas II affords only CDO^+ (m/e 30). The observation that II eliminates CHO as well as CDO (Table 2), and that in I the CHO loss is more pronounced than the CDO loss, does not necessitate H/D scrambling, since a metastable peak establishes the sequential loss of carbon monoxide and a hydrogen radical from the furan molecular ion. The carbon monoxide loss must involve a hydrogen rearrangement, and if this occurs to the β-carbon atom, as seems probable, then II could lose both CHO and CDO as depicted by the possible sequence II ⟶ d or d'. The results are consistent with competition between direct loss of CHO from furan and a sequential loss (viz. II ⟶ d or d').



The most abundant fragment ion in the 70ev mass spectrum of thiophen is due to an M - C_2H_2 species (*m/e* 58) and an abundant "metastable peak" is found for the *m/e* 84→58 transition at *m/e* 40.0. 2-d_1-Thiophen (III) undergoes the metastable transitions $M^+ \rightarrow M - C_2H_2$ and $M^+ \rightarrow M - C_2HD$ with equal probability as established by two metastable peaks of equal intensity at *m/e* 40.95 and 39.6 (see *e*), while 2,5-d_2-thiophen (IV) and 2,3-d_2-thiophen (V) both undergo the transitions $M^+ \rightarrow M - C_2H_2$, $M^+ \rightarrow M - C_2HD$ and $M^+ \rightarrow M - C_2D_2$ to give "metastable peaks" at *m/e* 41.8, 40.5 and 39.1 in the intensity ratio 1:4:1 (see *f*). These results establish that hydrogen scrambling occurs in thiophen in that form of the molecular ion undergoing acetylene elimination. The various "metastable peaks" referred to above are still observed in the same intensity ratios at a nominal 12ev, and at this beam energy the daughter ions for the possible transitions are observed in the same ratios as the "metastable peaks".(9) A second important fragmentation reaction (CHS^+ formation) is preceded by partial randomization {e.g., CHS^+ (22%) and CDS^+ (78%) from 2,5-d_2-thiophen (IV) at 70ev; scrambling increases at low ev, the ratio being CHS^+ (33%) and CDS^+ (67%) at 16ev}.



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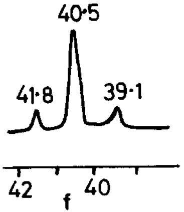

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In summary, the deuterium labelling results establish that either hydrogen randomization does not occur in furan prior to fragmentation, or is slow compared to the rate of fragmentation. In contrast, the hydrogens of thiophen are completely scrambled prior to the major fragmentation reaction (M - C_2H_2), and partially scrambled prior to CHS^+ formation. This difference in behaviour of the two heterocycles might simply be a consequence of the relative rates of potential scrambling *vs*. fragmentation reactions, but it is noteworthy that photo-induced rearrangement of arylthiophens involves an interchange of carbon atoms of the thienyl ring and is suggested to occur through a species which utilises the sulphur 3d electrons.(10) Hence, an analogous species could not be generated from a furan(10) and indeed diphenylfurans fail to undergo photochemically induced phenyl group migrations.(11) It is therefore tempting to suggest that there might be a similarity in the mechanism of photo-induced and electron impact-induced rearrangements of the thiophen nucleus.

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8. A finite amount of scrambling should produce some M - C_2D_2 ions ($C_2H_2O^{+\cdot}$) from II. However, the 13.5% of d_1-contaminant of II produces $C_2H_2O^{+\cdot}$ ions by loss of C_2HD; the correction factor for this reaction almost exactly accounts for the observed $C_2H_2O^{+\cdot}$ intensity (5 ± 2% of the total m/e 42 ions), but it is not sufficiently accurate to establish whether a finite loss of C_2D_2 occurs from isotopically pure 2,5-d_2-furan (II).
9. The analysis of daughter ion intensities is simplified in 12ev spectra, since the 12ev spectrum of thiophen itself contains no significant M - C_2H_3 ion.
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