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REARRANGEMENT IONS. IV.[1] MASS SPECTRUM OF THIOPHENE-2,5-$^{13}C_2$

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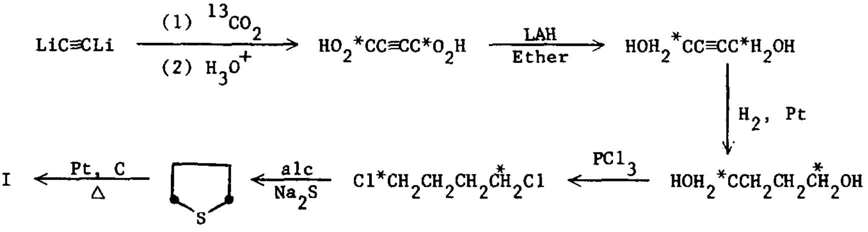
Electron impact-induced scrambling of aromatic hydrogen atoms has been shown to occur in benzene,[2] pyridine,[3] toluene,[4] thiophene,[5] and in many other classes of compounds.[6] However, reports of carbon scrambling (via C-13 labelling) in simple aromatic systems have been limited to benzene,[7] and several of its derivatives such as toluene,[1,8] phenol,[9] thiophenol,[9] and aniline.[10] Carbon scrambling in thiophene, and the lack of it in furan, has been suggested as a result of the examination of the mass spectra of arylthiophenes and arylfurans, respectively.[11] Recently, a study of the mass spectrum of benzo(b)thiophene-2-$^{13}C_2$ revealed that partial scrambling of the carbon atoms occurred prior to formation of many of the fragment ions, although a quantitative interpretation was not possible.[12]

The choice of an arylthiophene or a benzothiophene as a suitable model to predict the behavior of thiophene itself upon electron impact is not readily apparent. In view of this, thiophene-2,5-$^{13}C_2$ (I) has been synthesized, and label retentions in four major ions determined. Synthesis of (I) was achieved by the sequence outlined in Scheme I.[13]



Scheme I

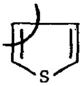
Spectra were recorded on an AEI MS-9 mass spectrometer at 70 eV, and at a resolution of 17,000 (10% valley definition); data represent averages of 10 readings. For the ions examined, the calculated values of label retentions expected for complete scrambling and no scrambling, as well as the observed values, are given in Table I.

CHS ion (m/e 45) - Label retentions establish that the formation of the CHS ion is preceded by partial scrambling only as evidenced by the abundant unlabelled CHS ion (no scrambling would produce ^{13}CHS ions only). A metastable peak[14] at 34.9 denoting the process $C_2H_2S^+ \longrightarrow CHS^+ + (13)$ provides another source of the 45 ion thereby complicating quantitative analysis. The observed retentions differ only slightly from those found for the common ions in the deuterated[5] and arylated[11] thiophenes.

C_3H_3 ion (m/e 39) - The formation of the 39 ion must involve extensive scrambling as evidenced by the abundance of the dilabelled ion, $^{13}C_2CH_3$. Although the data show that scrambling is not complete, the extent of scrambling is fairly close to that observed for the formation of the CHS ion.

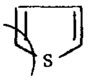
C_2H_2S ion (m/e 58) and C_3HS ion (m/e 69) - The carbon atoms involved in the formation of these ions are not known. Table I shows the theoretical values expected for complete scrambling and no scrambling via paths a-d as well as equal combinations of each. For either ion, the observed retention does not agree with the distribution expected for any one path. Regardless of the path operating, it is readily apparent that significant scrambling has occurred prior to formation of the 58 ion owing to the presence of unlabelled C_2H_2S ions. However, the observed retention does not allow conclusions to be drawn regarding the formation of the C_3HS ion except that scrambling, if it occurs, is not complete. If scrambling does not take place, path d appears to be favored over path b, although the data do not allow such a clear cut distinction amongst the various possibilities.

path a



path b

path c



path d

Hence, it may be concluded that prior to formation of the major ions, the carbon atoms in thiophene are partially scrambled. However, scrambling appears to be more complete at lower voltages (this effect is most dramatic in the formation of the CHS ion) than at higher voltages.[15] Because the CHS^+ ion, $C_2H_2S^+$ ion, and the C_3HS^+ ion have more than one origin, no quantitative conclusions can be drawn regarding the extent of rearrangement in thiophene prior to fragmentation. Scrambling may be envisioned as proceeding through a transition state or intermediate shown below.[16] Valence tautomerism to explain carbon scrambling in benzene has been suggested by Jennings[2] by analogy to known photochemical processes.

Studies on other 13-C heteroaromatic systems are currently in progress.

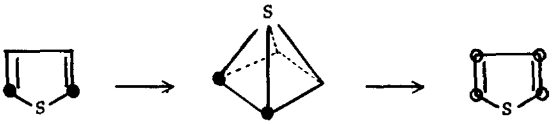


Table I. Mass Spectral Peaks (Observed and Calculated) for Thiophene-2,5-$^{13}C_2$

		Relative Abundance[e-g]						
m/e	Composition		Complete Scrambling			No Scrambling		Observed[h]
39	C_3H_3		none			none		.000
40	$^{13}CC_2H_3$		.500			all		.677 (.630)
41	$^{13}C_2CH_3$		.500			none		.323 (.370)
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45	CHS		.500			none		.298 (.391)
46	^{13}CHS		.500			all		.702 (.609)
——		a	c	a + c	a	c	a + c	
58	C_2H_2S	.167	.167	.167	none	none	none	.087 (.130)
59	$^{13}CCH_2S$	.667	.667	.667	none	all	.667	.729 (.684)
60	$^{13}C_2H_2S$	.167	.167	.167	all	none	.333	.184 (.186)
——		b	d	b + d	b	d	b + d	
69	C_3HS	none	none	none	none	none	none	.000 (.000)
70	$^{13}CC_2HS$	.500	.500	.500	none	all	.500	562 (.550)
71	$^{13}C_2CHS$	.500	.500	.500	all	none	.500	.438 (.450)

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[e] Corrected for naturally abundant ^{13}C. [f] Calculated for 100% isotope enrichment; sample contained 31.36% dilabelled thiophene, 19.36% unlabelled thiophene, and 49.28% monolabelled thiophene. [g] Σ each set = 1.000. [h] Obtained at 70 eV; values in parenthesis obtained at 20 eV.

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