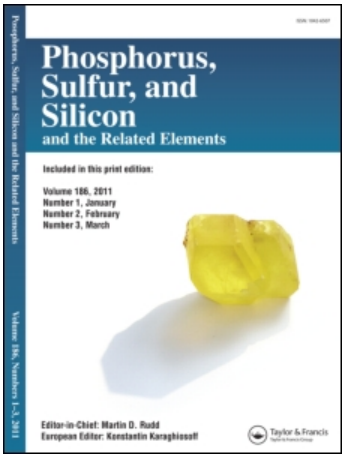

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ELECTRON IMPACT STUDIES ON NITROAROYLTHIOPHENES

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ELECTRON IMPACT STUDIES ON NITROAROYLTHIOPHENES

by

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ABSTRACT

A comparative electron impact study on 2-(2′-nitrobenzoyl)thiophene[1](1), 2-(2′-nitrobenzoyl)-3-methylthiophene[2](2) and the corresponding 4′-nitrobenzoyl derivatives (3 and 4)[3,4] is presented. The results suggest that the presence of nitro group β- to the carbonyl affects the general fragmentation pattern recorded in the literature for 2-acyl and 2-aroylthiophenes.

Literature records in detail the effect of electron impact on thiophene,[5] alkylthiophenes,[6,7] benzophenones,[8] 2-benzoylfurans,[9] 2-benzoylthiazoles,[10] 2-acyl and 2-aroylthiophenes.[11,12] There is however no report on the mass spectra of 2′-nitrobenzoylthiophenes and the purpose of the present study is to see whether there is any similarity in the mass spectral fragmentation of 2′-nitrobenzoylthiophenes and 4′-nitrobenzoylthiophenes to the reported fragmentation of simple aroylthiophenes.

The four nitrobenzoylthiophenes were prepared according to the procedure described in the literature[1–4] by the Friedel Crafts acylation of thiophene and 3-methylthiophene.

Mass spectral studies have established that these spectra are similer to that of acetophenone.[12] A comparison of the mass spectra of 2′-nitrobenzoylthiophenes (1 and 2) with benzoylthiophenes as well as 4′-nitrobenzoylthiophenes (3 and 4) indicated that while the characteristic features of 2-aroylthiophenes are still present in the fragmentation pattern of the nitro compounds, there are certain peculiarities, which can only be attributed to the participation of the nitro group in the fragmentation.[13]

The 4′-nitrobenzoylthiophenes 3 and 4 indicated the formation of the stable acylium cation at *m/e* 111(**3a**) and *m/e* 125(**4a**) as the base peak in their mass spectra. While this was in line with the observation with simple acyl and aroylthiophenes the corresponding fragments from compounds 1 and 2 were seen to the extent of only Σ_{26} of 12.7 and 4.5% total ion current intensity for the base peak intensity of 14.9 and 12.1 respectively. These correspond to 85 and 37% relative intensity, to the base peak. The base peak in the case of compound **1** was due to fragment **1b** at *m/e* 134 (Σ_{26} = 14.9) and in the case of compound 2 it was due to fragment **2b** at *m/e* 113 (Σ_{26} = 12.1). Fragment **1b** is still an acylium cation but formed through an intra-molecular transfer of an oxygen from the nitro group to the other half of the fragment. The resulting nitroso acylium cation possibly is resonance stabilised as represented in Chart I. This fragment **2c** is also formed from compound 2 but only to the extent of 8.84% total ion current. In the case of compound **2**, however, the base peak is not acylium cation but the counter part of the fragment **2c** *viz*, the fragment which has abstracted the oxygen from the nitro group intramolecularly before the fragmentation of the parent ion.

While Chart I gives a general representation, the difference in the location (or formation) of base peak due to the participation of nitro group in the fragmentation reaction,[13] in Chart II gives the two possible pathways A or B. It is recognized that the parent ion can be involved in two types of reaction, either by the interaction of the ortho nitro group in the oxidation of the thiophene sulphur to the sulfoxide state or in a carbon-hydrogen insertion reaction through a cyclic mechanism.

As indicated by the chart as well as the fragmentation pattern table (Table I), the fragments **1b/2c** undergo further fragmentation losing NO (to give *m/e* 104 Σ_{26} 12.3 and 8.84 in the spectra of compounds 1 and 2) as well as CO (*m/e* 106, Σ_{26} 0.87 and 0.68 respectively). Also both NO and CO might have been lost in succession forming the benzyne radical ion.[15] A careful analysis of the mass spectrum in the case of both compounds showed a feeble metastable peak between *m/e* 79–81 with maximum intensity in the 80–81 region. For the fragments **1b/2c** to undergo

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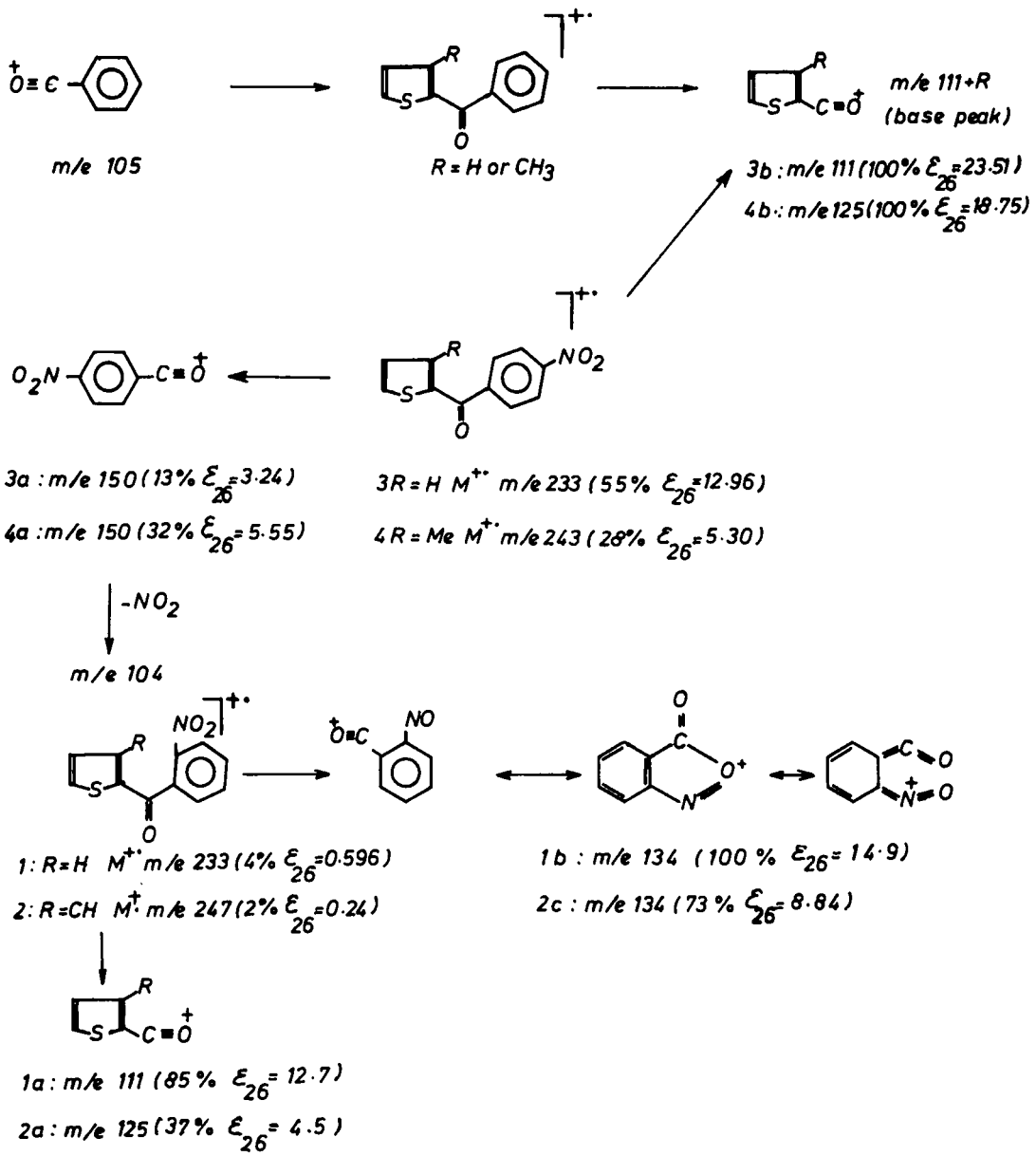
CHART 1



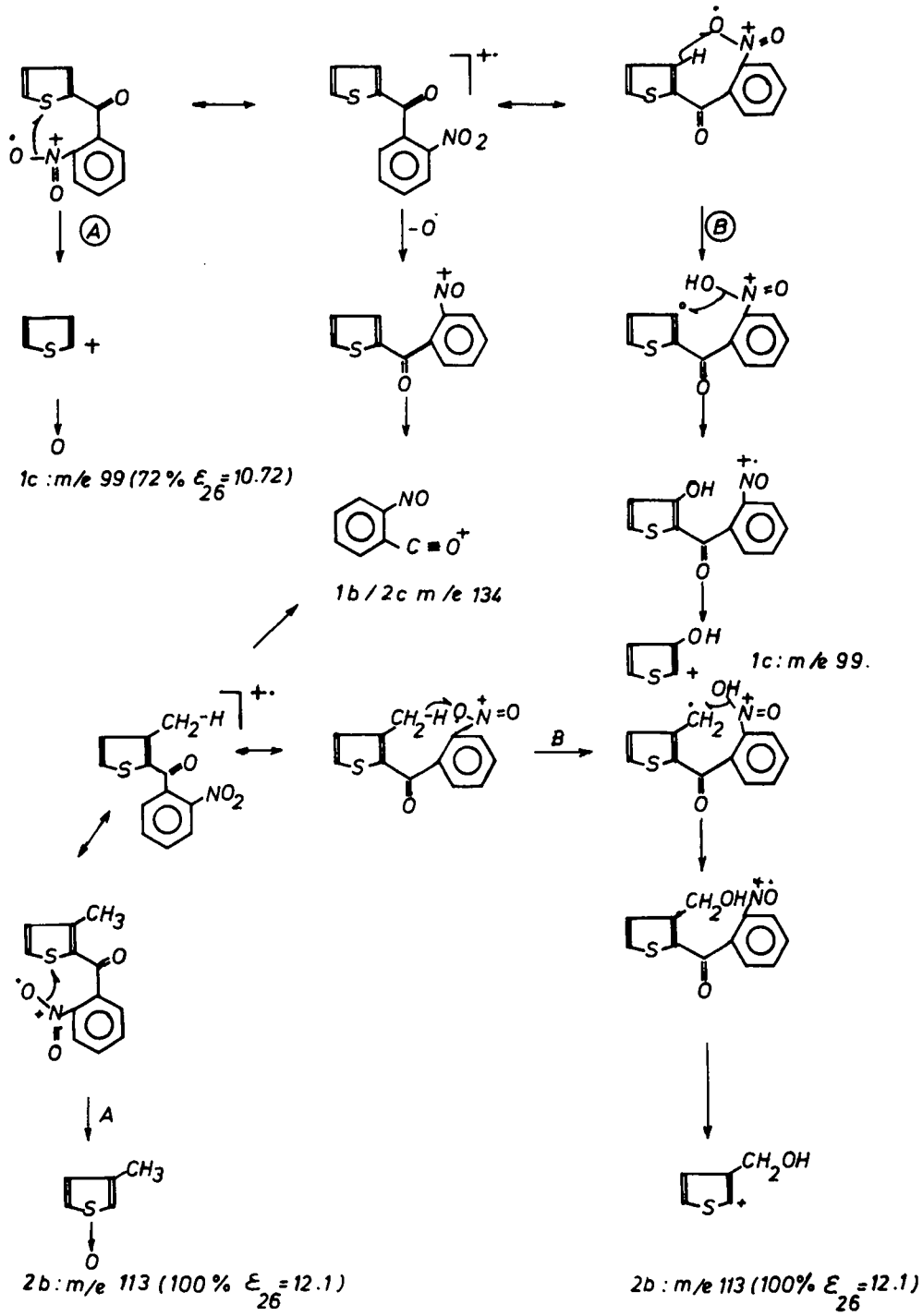
further fragmentation through loss of NO one can expect a metastable peak at *m/e* 80.716. Since both spectra indicate the metastable at this 80–81 region and as the intensity of *m/e* 104 is also good, this loss of NO from the fragments **1b**/2c can be taken as confirmed. There was also a metastable peak between 55 and 56 and the metastable expected for the transition *m/e* 104 to *m/e* 76 is 55.5. There was however no metastable peak in the region *m/e* 42-*m/e* 44. A metastable peak at 43.1 was expected for a simultaneous loss of both NO and CO from **1b**/2c to form the fragment *m/e* 76 and possibly this rules out such a

Also compound **1** apparently lost CO and CS with concomitant skeletal rearrangement giving fragment **1d** (*m/e* 161, $\Sigma_{26} = 0.09$) which further loses a molecule of NO_2 to give **1e** *m/e* 115, $\Sigma_{26} = 2.93$). The fragment **1g** could have been formed either directly from **1e** or rearrangement to **1f**. Chart III represents all these proposals.

Compound **2**, however showed a different set of fragments arising possibly due to the influence of the 3-methyl substituent on the thiophene ring in addition to the difference already noted. (Chart IV)

Though in Chart IV *m/e* 219 has been indicated by

CHART II



be a sulfoxide derivative, instead of the primary alcohol derivative. Though fragment **2b** (*m/e* 186, $\Sigma_{26} = 0.51$) and **2e** (*m/e* 189, $\Sigma_{26} = 0.25$) were seen, the possible intermediate fragments mentioned in the chart were not seen and these fragments can only be explained, by assuming skeletal rearrangements and the participation of nitro group. No metastable peak or *m/e* 186 were seen. Further the fragment **2f** at *m/e* 199 ($\Sigma_{26} = 0.3$) was explained through a simultaneous loss of oxygen and sulfur and fragments *m/e* 171 ($\Sigma_{26} = 2.29$) and **2c** at *m/e* 134 might have formed from **2f** as indicated by Chart IV. A metastable peak can be expected for the transition *m/e* 199 to *m/e* 171 at *m/e* 146.9 and one is actually present at

TABLE I

Percent total ion current Σ_{26}.

m/e	1	2	3	4
28	0.2	0.33	0.31	0.67
32	0.08	0.44	0.27	0.43
44	0.12	0.45	0.27	0.68
45	0.75	1.35	0.85	0.32
46	0.08	0.13		
50	1.3	1.34	0.78	0.74
51	1.2	1.8	0.27	1.11
52	0.2	0.65		
53	0.24	0.57		
71	1.2	0.45		
74	0.6	0.33	0.81	0.43
75	0.78	0.45	1.89	0.67
76	3.4	3.33	4.6	12.0
77	0.75	1.15	0.54	1.2
78	0.30	0.33	0.07	0.76
79	0.90	0.82		
81	0.32		0.27	
82	0.59	0.47	0.54	0.44
83	2.4	0.05	2.7	0.05
84	0.24	0.33		0.11
87	0.21	0.33		
88	0.63	0.40		
89	0.75	0.45		
97	0.08	2.94		3.75
98	0.80	0.33		0.60
99	10.72			0.31
100	0.55			
101	0.50	0.20		
102	0.20	0.20	0.10	0.14
103	1.8	0.08	0.27	0.08
104	12.3	8.84	3.51	3.75
105	1.1	0.65	0.5	0.42
109	0.22			
110	0.82	0.21	3.1	
111	12.7	0.456	23.51	0.15
112	0.8	0.98	2.38	0.09
113	0.66	12.1	0.89	
114	0.50	0.82	0.27	0.21
115	2.93	0.43	0.07	0.87
116	0.37			
117	0.29			
119	0.08			
121		0.33	0.81	
123		0.17		1.2
124		0.23		3.75
125		4.5		18.75
126		0.54		0.9
127		0.65		0.3
128		0.65		0.06

TABLE I (*continued*)

m/e	1	2	3	4
131	0.8	0.056		
132	0.25	0.08		
133	1.6	1.33		
134	14.9	8.84		
135	1.24	0.98		
150			3.24	5.55
151			0.54	0.86
157	0.9			
158	1.05			
159	0.20			
160	0.28			
161	0.9			
165	0.09			
170		0.33		
171		2.29		
172	0.44	0.72		
173	0.21	0.33		
174		0.33		
185	1.05		0.54	
186	1.05	0.48	0.54	0.21
187	0.67			0.06
189		0.25		
199		0.30		
200		0.60		0.05
201		0.33		1.5
217	0.58			
232	0.15	0.85	2.93	0.65
233	0.65	0.42	12.93	
234	0.05		1.89	
235			0.81	
246		0.08		0.96
247		0.24		5.30
248		0.06		0.51
249				0.06

List of metastable peaks:

1. Compounds **1** and **2** have a metastable at *m/e* 80-81. The decomposition of **1b/2c** *m/e* 134 to *m/e* 104 should give a metastable at 80.716.
2. Compounds **2** and **4** had a feeble metastable between 68-70 and for the decomposition of *m/e* 97 to *m/e* 82 the metastable should be 69.33.
3. Compound **1** alone showed a metastable between 133-135 and the metastable corresponding to the decomposition *m/e* 186 to *m/e* 158 is 134.3 and that due to *m/e* 185 to *m/e* 157 is 133.6
4. The decomposition of the ion *m/e* 199 to *m/e* 171 in compound **2** may be seen through a metastable at *m/e* 146.9. The spectrum has a metastable at this region *m/e* 146-148.
5. Compounds **3** and **4** have a feeble metastable ion peak at *m/e* 70-72. These may be due to the decomposition of ion *m/e* 150 to *m/e* 104. In fact the metastable peak in the case of compound **4** is rather broad starting from *m/e* 69 and the intensity increases to be maximum at *m/e* 71-72. The theoretical value for the metastable ion for the above process is *m/e* 72.04 and the broad metastable ion in the

CHART III

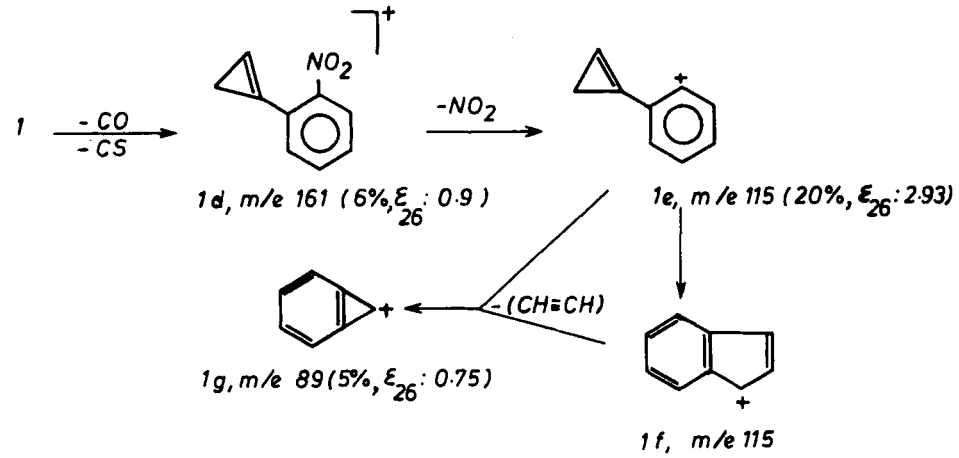


CHART IV

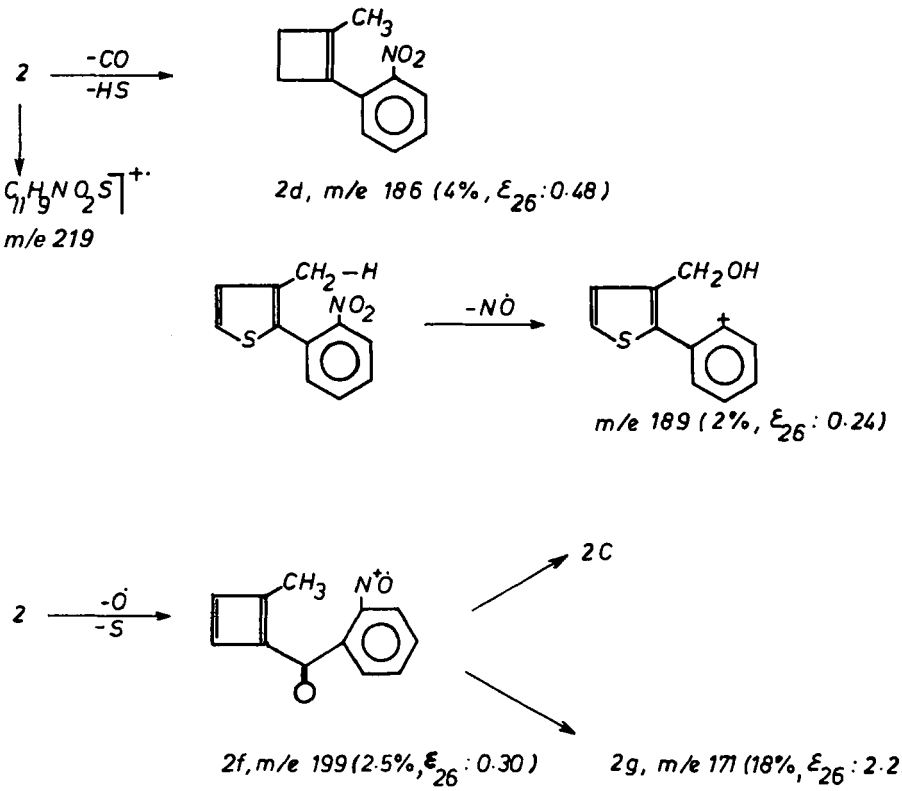


Chart V gives an entirely different pathway possible for the formation of fragments **2f** and **2j** and this chart also explains fragment **2k** which is not accounted for by the former.

Fragments corresponding to **2g** (*m/e* 200, 0.60) in the case of compound **1** should have been seen at *m/e* 186, if the fragmentation pattern were the same. Chart VI represents the fragmentation observed for compound **1**. A fairly wide metastable peak from that, one can anticipate two metastable peaks in this region, one at *m/e* 133.6 and a second at *m/e* 134.3 for the transitions *m/e* 185 to *m/e* 157 and *m/e* 186 to *m/e* 158. Further the peak *m/e* 82 is sharp and no metastable therefore is seen at 82.24 corresponding to the transformation *m/e* 158 to *m/e* 114.

Table I shows fragmentation patterns covering all the other fragments observed in the case of compounds **1** to **4** as well as the metastable peaks. The

CHART V

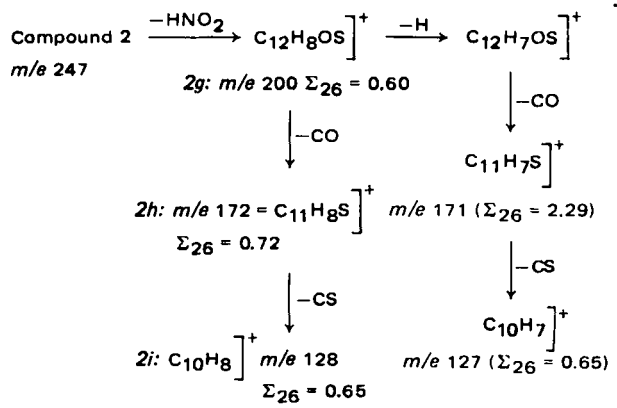
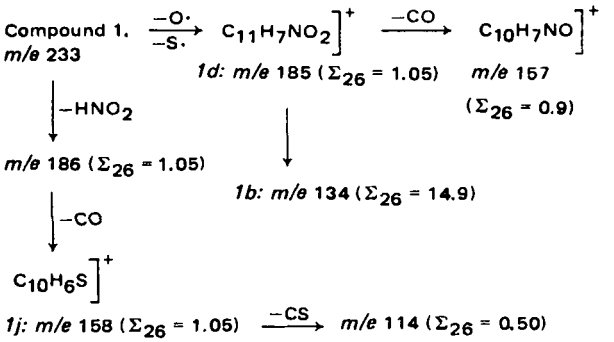


CHART VI



current and were calculated for peaks from *m/e* 26 to M + 2. The spectra were taken in a Varian CH-7 model instrument at 70 eV and filament current of 100 μA at an inlet temperature of 20°C.

A comparison of the various observations recorded here with the fragmentations recorded for compounds 3 and 4 in Chart I, clearly indicates that there is positive interference by the nitro group β- to the carbonyl. Further work is in progress to study the influence of other substituents as well as the mechanism of the nitro group participation.

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