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THE MASS SPECTRA OF SUBSTITUTED IMIDES[1]

SKELETAL REARRANGEMENTS ON ELECTRON IMPACT

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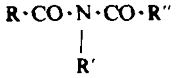
Abstract—The mass spectra of eighteen compounds of the general type R·CO N(R')·CO·R" have been investigated with the aid of deuterium labelling studies and high resolution measurements. The spectra exhibit pronounced skeletal rearrangement peaks, and in several cases the structures of the rearrangement ions have been definitely established.

ALTHOUGH the spectra of N-alkylsuccinimides[2] and phthalimides[3-5] have been reported, no survey (apart from our preliminary communication[6]) of the mass spectra of compounds of the type R·CO·N(R')·CO·R" has been reported. Because of recent interest[3,4,6-19] in electron impact induced losses of CO and CO_2 from carbonyl compounds by skeletal rearrangement processes of the type $ABC^{\dagger} \longrightarrow AC^{\dagger} + B$ (the loss of CO from quinones[20-24] should not be considered a skeletal rearrangement process,[cf. 18]) we have synthesized a series of imides, and this paper is primarily concerned with the geneses and structures of skeletal rearrangement fragments observed in their spectra.

The mass spectra of I–XVIII are recorded in Fig. 1–7 or Table 1. Exact mass measurements are listed in Table 2. The presence of a metastable ion in either the text or a figure is indicated by an asterisk.

The skeletal rearrangement ions in the spectra of I–XVI are summarized in Table 3. The compositions of these ions have been established by exact mass measurements (Table 2), and the processes are substantiated by metastable peaks in the spectra of I, II, XII, XIII, XIV and XV. It can be seen that large skeletal rearrangement ions are not observed in the spectra of compounds which may fragment through N-alkyl side chains (R' > Me; e.g. IV, V, VII and VIII), where R' is a substituent which favours the formation of a stable amine cation by the process $M^{+} \overset{-MeCO\cdot}{\longrightarrow} \overset{-CH_2CO}{\longrightarrow}$ (e.g. IX, X and XI), or when R' is a substituent which may itself form a stable cation (e.g. XV and XVI). Even when R" is Et (XII) the $M^{+} \overset{}{-} CO$ ion is pronounced (13% of the base peak) (Fig. 4). It is also noteworthy that the mass spectrum (Table 1) of N,N'-diacetylurea (XVII) does not contain any skeletal rearrangement ions. As a general rule, skeletal rearrangement ions are observed in the mass spectra of imides when simple fragmentations are not favoured.

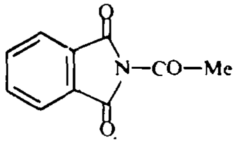


$$\mathrm{R{\cdot}CO{\cdot}\underset{\displaystyle R'}{\underset{|}{N}}{\cdot}CO{\cdot}R''}$$

	R	R′	R″
I	Me	H	Me
II	Me	Me	Me
III	CD_3	Me	CD_3
IV	Me	nPr	Me
V	Me	nBu	Me
VI	CD_3	nBu	CD_3
VII	Me	isoBu	Me
VIII	Me	secBu	Me
IX	Me	allyl	Me
X	Me	Ph	Me
XI	Me	CH_2Ph	Me
XII	Me	H	Et
XIII	Me	H	Ph
XIV	Ph	H	Ph
XV	Ph	Ph	Ph
XVI	Ph	CH_2Ph	Ph

MeCO·NH·CO·NH·CO·Me·

XVII



XVIII

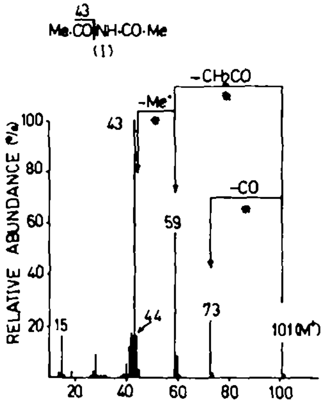


Figure 1

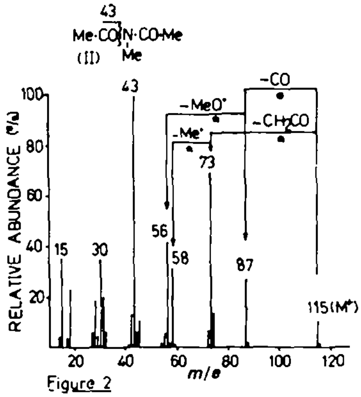


Figure 2

TABLE 1*. MASS SPECTRA OF COMPOUNDS IV, VII–XI, XIII–XVII

IV *m/e*	15	26	27	28	29	30	39	40	41	42	43	44	54	55	56	58	73	77	83	84
I(%)	40	8	43	24	28	22	21	7	23	46	100	10	7	6	10	10	4	17	6	6
	86	100	101	102	114	115	128	143(M)												
	8	6	3	2	3	3	8	3												
VII *m/e*	15	27	28	29	30	39	41	42	43	55	56	57	58	60	72	73	84	100	102	
I(%)	21	14	8	14	87	10	20	10	100	8	9	6	10	16	82	15	38	11	36	
	103	114	115	142	157(M)															
	3	9	5	3	2															
VIII *m/e*	15	27	28	29	39	40	41	42	43	44	45	55	56	57	58	60	72	84	86	87
I(%)	24	20	15	41	20	14	78	20	100	76	10	15	20	18	20	20	10	16	44	7
	97	100	102	114	128	142	157(M)													
	7	7	22	9	9	2	1													
IX *m/e*	15	27	28	39	41	42	43	54	56	57	98	99	113	141(M)						
I(%)	16	10	12	22	15	18	100	7	26	15	5	8	2	1						
X *m/e*	43	51	65	66	77	93	94	117	135	136	177(M)									
I(%)	23	5	5	4	15	100	6	10	66	6	5									
XI *m/e*	39	42	50	51	63	65	77	78	79	89	90	91	92	104	106	107	131	148	149	
I(%)	11	5	6	15	7	18	20	8	25	6	5	34	6	6	100	16	3	38	20	
	191(M)																			
	17																			
XIII *m/e*	38	39	42	43	50	51	74	75	76	77	78	104	105	106	134	135	146			
I(%)	4	6	5	43	16	38	6	6	13	64	11	10	100	10	6	10	2			
	163(M)	164																		
	40	8																		
XIV *m/e*	39	50	51	76	77	78	94	104	105	106	148	197	225(M)	226						
I(%)	4	10	30	6	65	6	3	5	100	9	2	10	38	8						
XV *m/e*	39	50	51	65	76	77	78	105	106	197	198	273	301(M)							
I(%)	10	6	23	9	3	63	6	100	8	48	10	3	1							
XVI *m/e*	39	50	51	65	76	77	78	79	91	104	105	106	210	211	212	315(M)				
I(%)	8	8	26	10	5	64	8	6	16	8	90	32	35	100	18	1				
XVII *m/e*	28	40	41	42	43	44	59	70	85	102	129									
I(%)	16	6	13	25	100	40	60	34	16	2	2									

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[*] All ions greater than 2% of the base peak (arbitrarily 100%) are recorded. Several molecular ions which are less than this value are also recorded.

TABLE 2. EXACT MASS MEASUREMENTS IN THE MASS SPECTRA OF I–XVIII

Compound	m/e	Composition
I	73	C_3H_7NO
	44	CH_2NO
	43	C_2H_3O
	42	C_2H_4N
II	87	C_4H_9NO
	73	C_3H_7NO
	58	C_2H_4NO
	56	C_3H_6N
	43	C_2H_3O
	31	CH_5N
	30	CH_4N
IV	115	$C_6H_{13}NO$ (70%) $C_5H_9NO_2$ (30%)
	114	$C_5H_8NO_2$
	102	$C_4H_8NO_2$ (60%) $C_5H_{12}NO$ (40%)
	101	$C_5H_{11}NO$ (95%) $C_4H_7NO_2$ (5%)
	100	$C_5H_{10}NO$
	86	C_4H_8NO (55%) $C_3H_4NO_2$ (45%)
	83	C_5H_9N
	84	C_4H_6NO
	72	C_3H_6NO
	58	C_3H_8N
	56	C_3H_6N (60%) C_2H_2NO (40%)
	43	C_2H_3O (90%) C_3H_7 (10%)
V	128	$C_6H_{10}NO_2$
	115	$C_6H_{13}NO$ (90%) $C_5H_9NO_2$ (10%)
	114	$C_6H_{12}NO$ (85%) $C_5H_8NO_2$ (15%)
	102	$C_4H_8NO_2$
	100	$C_5H_{10}NO$
	87	C_4H_9NO
	86	C_4H_8NO (65%) $C_3H_4NO_2$ (35%)
	84	C_4H_6NO
	73	C_3H_7NO
	72	C_3H_6NO (80%) $C_4H_{10}N$ (20%)
	60	C_2H_6NO (80%) $C_2H_4O_2$ (20%)
	43	C_2H_3O (95%) C_3H_7 (5%)
	30	CH_4N
VII	115	$C_6H_{13}NO$
	114	$C_6H_{12}NO$ (50%) $C_5H_8NO_2$ (50%)
	102	$C_4H_8NO_2$
	100	$C_5H_{10}NO$
	84	C_4H_6NO

TABLE 2.—*continued*

Compound	*m/e*	Composition
VII	72	C_3H_6NO (90%) $C_4H_{10}N$ (10%)
(*continued*)	60	C_2H_6NO (80%) $C_2H_4O_2$ (20%)
	43	C_2H_3O (90%) C_3H_7 (10%)
	30	CH_4N
VIII	128	$C_6H_{10}NO_2$
	97	$C_6H_{11}N$
	86	C_4H_8NO
IX	113	$C_6H_{13}NO$
	99	C_5H_9NO
	98	C_5H_8NO
	57	C_3H_7N
	56	C_3H_6N
	43	C_2H_3O
X	135	C_8H_9NO
	117	C_8H_7N
	93	C_6H_7N
XI	131	C_9H_9N
XII	87	C_4H_9NO
	73	C_3H_7NO
	60	C_2H_6NO
	57	C_3H_5O
	43	C_2H_3O
XIII	135	C_8H_9NO
	134	C_8H_8NO
XIV	197	$C_{13}H_{11}NO$
	94	C_6H_6O
XV	273	$C_{19}H_{15}NO$
XVI	211	$C_{14}H_{13}NO$
XVIII	148	$C_8H_6NO_2$
	147	$C_8H_5NO_2$
	105	C_7H_5O
	104	C_7H_4O
	103	C_7H_5N
	90	C_6H_4N

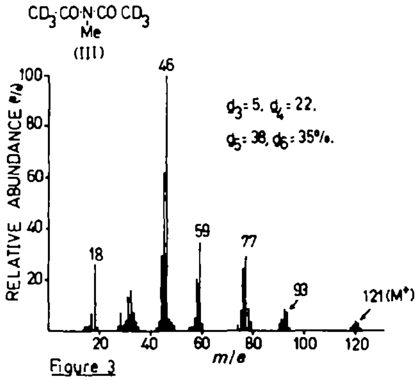


Figure 3

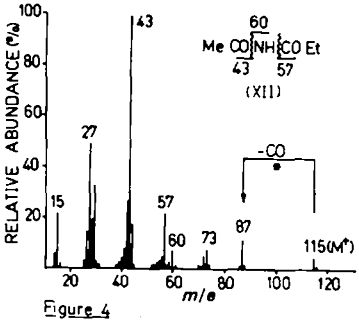


Figure 4

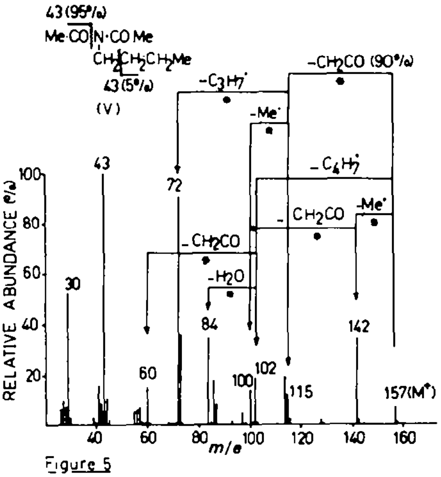


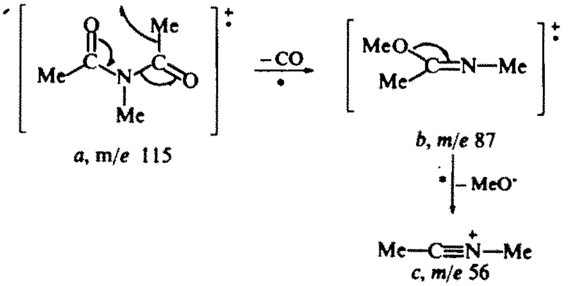
Figure 5

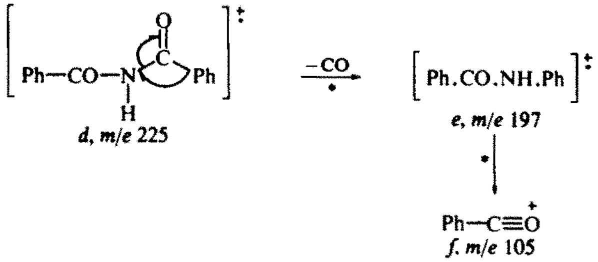
TABLE 3. RELATIVE ABUNDANCE (%) OF M^+—CO IONS IN THE SPECTRA OF I–XVI

Compound	I	II	IV	V	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
M^+—CO	24	28	2	—	—	—	3	—	—	13	11	10	3	—

It is possible to follow the decomposition of the skeletal rearrangement ion in the spectrum (Fig. 2) of II, and therefore to determine the site of migration of the Me group. The interpretation has been aided by the spectrum (Fig. 3) of the d_6 derivative III. The rearrangement process M^+—CO—MeO· is substantiated by metastable ions, and indicates Me migration to oxygen, possibly by the process *a* → *c*. A similar process is observed in the mass spectrum (Fig. 1) of diacetamide I, but here, loss of MeO· from the M^+—CO species is not substantiated by a metastable peak. It is reasonable to assume that oxygen is the migration site of the rearrangement process (M^+—CO) in the mass spectra of those imides where R and R″ = Me or Et, even though it cannot be proven in the majority of cases.

A different situation is observed in the mass spectrum (Table 1) of XIV, where the M^+—CO ion (*e*, *m/e* 197) decomposes by loss of PhNH· (substantiated by a metastable ion at *m/e* 56·0) to the benzoyl cation (*f*, *m/e* 105), indicating phenyl migration to nitrogen (*d* → *e* → *f*).





It has been shown (*vide supra*) that imides, on electron impact, may lose CO with concomitant rearrangement of the incipient radical either to oxygen (R = R″ = Me) or nitrogen (R = R″ = Ph). The presence of such processes limits both *a priori* predictions of fragmentation modes and the application of the "element mapping" technique[25–27] to this class of compound.

The normal decomposition modes of I–XVII are unexceptional, and specific examples are summarized in Figs. 1–6. Some of the general features may be illustrated

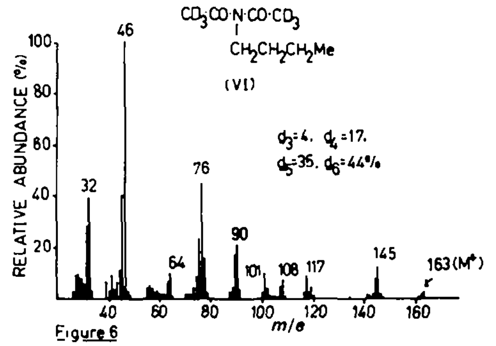


Figure 6

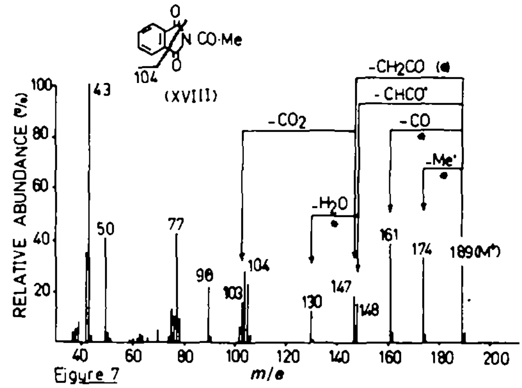
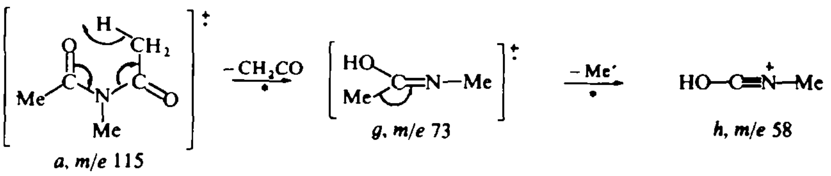


Figure 7

by a consideration of the spectra of II and V (Figs. 2 and 5) and of their d_6 derivatives III and VI (Figs. 3 and 6). The base peak of the spectrum of II is the acetyl cation (*m/e* 43) as is the case with the N-substituted imides II–IX. The other major process in the spectrum of II is M^+—CH_2CO—Me·. The Me radical lost in this process is that adjacent to the carbonyl group (Fig. 3), and as there is no evidence to suggest that the M^+—CH_2CO ion (*m/e* 73) decomposes by loss of MeNH· to the acetyl cation (*m/e* 43), we have a marginal preference for hydrogen rearrangement to oxygen (i.e. *a* → *g* → *h*) which is analogous to the behaviour of β-diketones.[9]

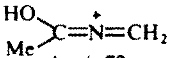


The spectra of the propyl and butylimides (IV–VIII) are complex, and extensive high resolution measurements (Table 2) were necessary for their interpretation. The mass spectrum (Fig. 5) of the n-butyl derivative V, illustrates this feature. Three major fragmentation processes operate, *viz.* (A) M^+—Me·—CH_2CO (to *m/e* 100), (B)

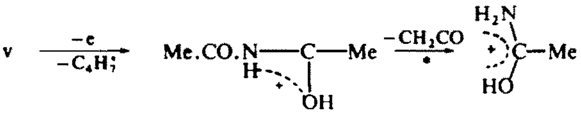
$M^+—CH_2CO—C_3H_7\cdot$ and other combinations (to *m/e* 72), and (C) $M^+—C_4H_7\cdot—CH_2CO$ (to *m/e* 60). Other variations of these modes are outlined in Figs. 5 and 6. The Me radical lost in process A is that adjacent to carbonyl (Fig. 6), and consequently *m/e* 100 is best represented as *i*. If the loss of ketene in process B proceeds *via* a favoured 6-membered transition state (McLafferty rearrangement),[28, 29] then *m/e* 72 may be represented as *j*. The $M^+—C_4H_7\cdot$ ion (*m/e* 102) occurs to the extent of 18–36% of the base peak (*m/e* 43) in the spectra of the three butyl isomers V, VII and VIII, whereas the corresponding $M^+—C_3H_5\cdot$ ion (*m/e* 102) constitutes only 1% in that of the n-propyl compound IV. Such processes do not occur in the spectra of substituted β-diketones,[9] but are observed in those of alkylbarbiturates.[30] Process C may then be represented by the Scheme V → *k* → *l*. The sec-butyl derivative VIII may be distinguished from the n- and iso-butyl compounds V and VII, by the presence of a prominent $M^+—Et\cdot$ cation (10% of the base peak) in the spectrum of VIII.

$$n\text{-}C_4H_9\text{—NH—C}\equiv\overset{+}{O}$$

i, *m/e* 100



j, *m/e* 72



k, *m/e* 102 *l*, *m/e* 60

Finally, it is of interest to consider the spectrum (Fig. 7) of N-acetylphthalimide (XVIII). Many of the fragmentation modes in this spectrum are unexceptional and are indicated in Fig. 7. However, the remarkable loss of CO_2 from phthalimides on electron impact[3,4] is also observed in this spectrum, viz. the process $M^+—CH_2CO—CO_2$ to *m/e* 103 ($C_7H_5N^+$) (Fig. 7). This certainly means that the $M^+—CH_2CO$ ion (*m/e* 148) has the structure of the phthalimide radical ion, i.e. in this case, elision of ketene has occurred with concomitant hydrogen rearrangement to nitrogen.

EXPERIMENTAL

All mass spectra (except that of XIV) were determined with an Hitachi Perkin-Elmer R.M.U. 6D mass spectrometer with a source and inlet temp of approximately 150°. Compound XIV (which decomposed under the above conditions) was determined by the direct insertion technique at 60°. Exact mass measurements were determined with an A.E.I. MS 9 mass spectrometer using a resolution of 14,000 (10% valley definition) and heptacosafluorotributylamine provided the reference masses. All measurements were correct to within 15 ppm.

The purity of all samples was routinely checked by VPC and NMR spectroscopy. Compound II was a purified commercial sample. The following compounds were prepared by reported procedures: I,[31] V,[32] IX,[33] X,[34] XI,[35] XII,[36] XIII,[36] XIV,[37] XV,[33] XVI,[38] XVII[39] and XVIII.[40]

Compounds IV, VII and VIII were prepared by the following general synthesis.

The amine (0·25 mole) was added dropwise over a period of 30 min to Ac_2O (250 ml), keeping the temp below 5°. The reaction mixture was then heated under reflux for 1 hr, whereafter the apparatus was arranged for distillation. Over a period of 10–20 hr a mixture of $AcOH\text{–}Ac_2O$ was distilled off through a

15 × 0·6 cm packed column at atm press. The various products were obtained (in almost quantitative yield) by vacuum distillation, and were further purified by preparative VPC. Their purity was checked by NMR spectroscopy.[41]

Compound	B.p.	%C	%H	%N
IV	84°/10 mm	Found 58·62 Calc. 58·72	9·22 9·15	10·04 9·78
VII	87°/10 mm	Found 61·55 Calc. 61·12	9·93 9·62	—
VIII	86°/12 mm	Found 61·23 Calc. 61·12	9·71 9·62	9·08 8·91

Labelled samples

(a) *Compound* III. $MeNH_2 . HCl$ (1·0 g) and Ac_2O-d_6 (3·0 ml) were refluxed for 3½ hr. The pure product was obtained by preparative VPC.

(b) *Compound* VI. n-Butylamine (0·9 ml) was slowly dropped onto a mixture of Mg turnings (300 mg) and Ac_2O-d_6 (2·24 g). After heating under reflux for 3½ hr, the product was obtained by preparative VPC.

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