MASS SPECTROMETRIC STUDIES—VII¹ BENZYLIDENEMALONAMIDE AND RELATED COMPOUNDS

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Abstract—The product of base-catalysed condensation of benzaldehyde and malonamide is the complex Schiff base β -(benzylideneimino)benzylmalonamide, rather than benzylidenemalonamide as previously reported. Analogous Schiff bases are formed from aliphatic as well as aromatic aldehydes. Benzylidenemaloanamide itself is formed from β -(benzylideneimino)benzylmalonamide by treatment with BF₃. The mass spectra of this compound and the Schiff bases are analysed.

RECENTLY we discussed the mass spectra of some benzylidenemalonic acids and showed that the major fragmentations follow impact-induced dehydration to a benzylidenemalonic anhydride.² We were interested to examine the behaviour of the corresponding benzylidenemalonamides under electron impact, and in particular to see if ammonia was lost to produce a benzylidenemalonimide radical cation. The synthesis of benzylidenemalonamide (1) from benzaldehyde and malonamide in the presence of aqueous sodium hydroxide was first reported by Heuck,³ and has apparently been repeated on two subsequent occasions.^{4, 5} In our hands the preparation appeared to give the compound reported as 1, but its mass spectrum (M⁺ 295, $C_{17}H_{17}N_3O_2$) was clearly incompatible with this structure. Of several alternative formulations, the Schiff base structure 2 or the azetidine 3 were considered most likely for this compound, but only 2 agreed with all the physical data.

Thus with neutral D_2O the compound exchanges four protons, and then a fifth one rather more slowly. In its mass spectrum it shows a strong ion $(C_{14}H_{12}N^+)$ at m/e194, which is not displaced on deuterium exchange; this is consistent with the presence of the group $-CH(CONH_2)_2$, containing all the exchangeable H atoms and capable of being lost as a single fragment after electron impact. The spectrum does not contain ions corresponding to the usual azetidine cross-ring fissions (lines "a" and "b" in 3). The full mass spectrum is considered in more detal later. The NMR spectrum shows the expected multiplet of ten aromatic protons, a broad one-proton singlet at δ 6.79 from the single benzylidene proton, and an AX system centred at δ 5.45 and 4.41, together with a readily exchangeable four-proton signal (δ 3.42) from the amide groups.

The formation of 2 is thought to result from addition of ammonia (liberated by hydrolysis of amide groups) to the initially-formed benzylidenemalonamide (1), followed by Schiff-base formation with excess benzaldehyde:

$$\begin{array}{c} Ph - CHO + CH_{2}(CONH_{2})_{2} \xrightarrow{OH} Ph - CH = C(CONH_{2})_{2} \\ & & 1 \\ & & 1 \\ Ph - CH - CH(CONH_{2})_{2} \xrightarrow{PhCHO} Ph - CH - CH(CONH_{2})_{2} \\ & & | \\ N = CHPh \\ & NH_{2} \\ & 2 \end{array}$$

As would be expected, addition of extra ammonia results in a very marked increase in yield of 2 and in fact no other base than ammonia need be used to bring about the condensation. No product was isolated when ammonia was replaced with methylamine or triethylamine.

The Schiff base 2 is also produced from dimethyl benzylidenemalonate (4) and ammonia. This reaction thus clearly takes place in several steps, and an intermediate such as 5 may be involved.



The Schiff base 2 is converted to the required benzylidenemalonamide 1 by treatment with boron trifluoride etherate in anhydrous dioxan:



Compound 1 prepared in this way has the expected physical properties. Its melting point is significantly lower than that claimed for this structure by Heuck,³ whose compound was originally characterized only by nitrogen analysis; as the figures expected for structures 1 and 2 differ by only 0.6%, we consider that all compounds previously reported as 1 are in fact 2. Although we have made many attempts with a wide range of conditions, we have been unable to prepare 1 directly by base-catalysed

condensation of malonamide and benzaldehyde. It is interesting to note that the corresponding furfurylidenemalonamide (6) can be prepared by carefully-controlled base-catalysed condensation of furfural and malonamide. With malonamide and excess of ammonia, the furan analogue (7) of the Schiff base 2 is formed:



Acetaldehyde, propionaldehyde and n-heptaldehyde gave only Schiff bases when treated with ammonia and malonamide. With salicylaldehyde, coumarin-3-carbox-amide was formed; the analogous reaction occurs with malonic acid to give coumarin-3-carboxylic acid.⁶

The polyfunctional nature of 2 suggests its potential value in heterocyclic synthesis, and experiments directed to its cyclization are in hand.

Mass spectrometry

(i) Benzylidenemalonamide and furfurylidenemalonamide. The mass spectrum of benzylidenemalonamide (1) has as base peak the M - 1 ion, and the spectrum of the tetradeutero-derivative of 1 shows that the ion originates mainly from loss of a non-exchangeable H atom. It seems likely that the chromenyl cation 1a is formed, similar processes having been shown to occur with related esters and ketones.⁷⁻⁹ Loss of NH₃ from the molecular ion is not such an important process as is loss of water from the corresponding acid, and the spectrum of the tetradeutero-derivative shows losses of both ND₃ and ND₂H, suggesting formation of the imide (1b) and cyclopentenone (1c) radical cations. Further fragmentations and shifts on deuteration are in agreement with these assignments and are summarized in Scheme 1 below. Loss of NH₃ from the M - 1 ion (1a) is best formulated as an "ortho effect" resulting in formation of the β -lactam 1d or its tautomer 1e.

Analogously to dimethyl benzylidenemalonate,¹ benzylidenemalonamide gives a rearrangement ion at m/e 106 resulting from migration of an amino group. The ion undergoes the expected shift to m/e 108 in the spectrum of the tetradeutero compound:







Furfurylidenemalonamide (6) fragments in a similar way to the benzylidene compound, except that no significant M - 1 ion is formed, showing that cyclization (analogous to $1 \rightarrow 1a$) does not occur in this system. (The ion at m/e 152 corresponds presumably to elision of CO from the furan ring.¹⁰)

(ii) Schiff bases. The mass spectra of the Schiff bases described in this paper are complex, and all show many competing fragmentation pathways. As mentioned, these compounds exchange the four amide protons with neutral deuterium oxide more rapidly than they do the fifth proton, which is situated ∞ to the two amide groups. From consideration of the spectra of these pairs of deuterated derivatives, together with high-resolution measurements, the main fragmentations have been rationalized, and those suggested for the phenyl compound are set out in Scheme 2. It should be emphasized that many ion structures must be regarded as tentative, particularly when cyclizations involving non-labelled H atoms are postulated. Rationalization is further made difficult by the paucity of metastable ions in the spectrum of this compound. It is surprising that the base peak of the spectrum (m/e 146) requires the formulation shown, with the positive charge residing upon an sp²-hybridized C atom, but this is the only simple structure compatible with the labelling data. It will be recalled that an ion of apparently the same structure is prominent in the spectrum of benzylidenemalonamide, but the m/e 146 ion in that case decomposed to m/e 129 by loss of NH₃. It may be that here, on account of the many decomposition pathways available to the molecular ion of 2 the m/e 146 species is formed with too little excess energy to decompose further. The ions at m/e 104 and 105 ($C_2H_6N^+$ and $C_2H_7N^+$) presumably formed from the molecular ion by benzylic fissions without hydrogen transfer and with hydrogen transfer respectively. The ion at m/e 106 (C₇H₈N⁺) shifts to m/e 108 in the spectra of both the tetra and penta deuterated compounds, and may well be formed by successive 6-centre H transfers:



(It is also possible to write a mechanism involving NH_2 group migration. The two could be distinguished only by ¹⁵N-labelling.)

The mass spectra of the furan analogue (7) of 2 and its tetra and pentadeutero derivatives are recorded (Table 1); the fragmentations occurring can be rationalized in essentially the same way as those of 2.

The mass spectra of the Schiff bases from aliphatic aldehydes are even more complex. They contain many sets of isobaric ions (Table 2), and here also too few pathways are substantiated by metastable ions for complete rationalization of the spectra to be possible. Loss of the group $CH(CONH_2)_2$ is much less important in this series, no doubt on account of the absence of benzylic stabilization in the ions produced. The spectra are marked by a number of interesting rearrangements involving NH_2 -group migrations, and these are exemplified in the rationale (Scheme 3) suggested for the spectrum of the Schiff base (8) from acetaldehyde. The main fragmentations in the



spectrum of the Schiff base (9) from propionaldehyde resemble those of 8 and will not be discussed further. The spectrum of the Schiff base (10) from n-heptaldehyde is dominated by the $M - C_6H_{13}$ ion (*m/e* 226) and its further decomposition. As with the Schiff bases 8 and 9, it is assumed that the alkyl group attached to the azomethine linkage is lost, to produce the stable cation 10a. This fission is no doubt facilitated in this case by the greater stability of the alkyl radical lost. Further decomposition of 10a parallels that of the analogous species (*m/e* 156) in the spectrum (Scheme 3) of the Schiff base (8) from acetaldehyde, except that one extra pathway, in which 10a shows concerted loss of HCN and HOCN, becomes apparent. A possible mechanism consistent with the labelling data is shown in Scheme 4.

EXPERIMENTAL

All mass spectra were determined with an AEI MS9 spectrometer operating at 70 eV. Samples were introduced by the direct insertion technique. Exact masses were determined at a resolving power of 25,000 (10% valley definition) with ions in the spectrum of heptacosafluorotributylamine as references. NMR spectra were determined on a Varian HA 100 instrument, and IR spectra on Perkin-Elmer 137 and 457 instruments. M.ps are uncorrected.



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SCHEME 4

CH_{3}(CH_{2})_{5}-CH--CH(CONH_{2})_{2}^{-1}^{+} \cdot \\ N=CH-(CH_{2})_{5} CH_{3}

10, M<sup>+</sup>, m/e 311(315, 316) (5%)

\downarrow - CH_{3}(CH_{2})_{5}

H_{-} \cdot NH_{-} COH_{-} CONH_{2} \xrightarrow{-(HCN + HCNO)} CH_{3}(CH_{2})_{5}-CH_{2}-CH_{-}CONH_{2}

\downarrow - CH_{3}(CH_{2})_{5}-CH_{-} -CH_{-} CONH_{2} \xrightarrow{-(HCN + HCNO)} m/e 156 (159, 160) (26\%)
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10a, m/e 226(230, 231) (100%)

β -(Benzylideneimino)benzylmalonamide (2)

(a) Benzaldehyde (10 g) was added to a soln of malonamide (10 g) in water (10 ml). 2:0M NaOH (0:2 ml) was added and the mixture was stirred for 12 hr. The Schiff base 2 (0:13 g) was crystallized from MeOH to give prisms, m.p. 199-200°. (Found: C, 68:9; H, 5:7; N, 139. $C_{17}H_{17}N_3O_2$ requires: C, 69:2; H, 5:8; N, 14:2%); NMR Aromatic protons: multiplet from δ 7:2-76 (10H); benzylidene proton: broad singlet at δ 6:78 (1H); AX system centred at δ 5:45 and 4:41 (2H, J = 9 Hz); amide protons at δ 3:42 (4H); *IR spectrum* (above 1500 cm⁻¹, KCl disc) v_{max} 3350, 3250, 3060, 2890, 2830, 1690, 1650 (s), 1595 cm⁻¹.

(b) The same compound was prepared in 70-80% yield by shaking benzaldehyde (10 mole) and malonamide (10 mole) in an excess of aqueous ammonia (0.880) until a heavy ppt appeared (about 15 min). The reaction mixture was allowed to stand overnight at room temp and the base was crystallized from MeOH as before.

Benzylidenemalonamide

Compound 2 (19 g) and 48% BF₃-etherate (0.57 g) were heated under reflux in pure dioxan (125 ml) for 3 hr. The reaction mixture was cooled to room temp and added to water (500 ml). The resultant soln was extracted with ether, and the extracts were dried (MgSO₄) and evaporated to give *benzylidenemalona-mide*, crystals from EtOAc, m.p. 178-179°. (Found: C, 62.9; H, 5.6; N, 14.5. C₁₀H₁₀N₂O₂ requires: C, 63.2; H, 5.3; N, 14.7%; *IR spectrum* (above 1500 cm⁻¹, KCl disc) v_{max} 3380, 3150, 1687, 1660 (s), 1580 cm⁻¹.

 β -(*Furfurylideneimino*)/*furfurylmalonamide* (7) was prepared under the conditions described for the phenyl analogue, as prisms from MeOH, m.p. 183:5-184:5°. (Found C, 56:6; H, 5:0; N, 14:8, C₁₃H₁₃N₃O₄ requires: C, 56:7; H, 4:8; N, 15:2%).

Furfurylidenemalonamide (6), m.p. $205-208^{\circ}$, was prepared from furfural, malonamide and NaOEt as described by Heuck.³

Coumarin-3-carboxamide, m.p. 280-281° (lit.¹¹ m.p. 268-269°) was formed when salicylaldehyde and malonamide were condensed by the method described for benzaldehyde.

Schiff bases from aliphatic aldehydes

The conditions used for the preparation of the phenyl compound 2 from benzaldehyde, malonamide and ale nonia were used here also.

 β -(*Ethylideneimino*)ethylmalonamide (8) gave prisms from dioxan/water, m.p. 218-220°. (Found C, 493; H, 80; N, 243. C₇H₁₃O₂N₃ requires: C, 491; H, 76;; N, 246%).

 β -(Propylideneimino)propylmalonamide (9) gave prisms from dioxan/water, m.p. 199–201°. (Found C, 54'3; H, 8'0; N, 20'7. C₉H₁₇Q₂N₃ requires: C, 54'3; H, 8'5; N, 21'1%).

 β -(Heptylideneimino)heptylmalonamide (10) gave prisms from MeOH, m.p. 160–163°. (Found C, 657; H, 106; N, 135. C₁₇H₁₃O₂N₃ requires: C, 656; H, 107; N, 135%).

TABLE 1. LOW RESOLUTION MASS SPECTRA

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6	m/e	69	4	51	52	53	65	8	78	80	81
	I(%)	74	33	16	25	13	39	13	13	14	14
		83	86	91	92	93	94	95	96	109	120
		9	6	œ	13	20	55	55	69	6	6
		121	122	135	136	137	138	147	148	163	173
		4	38	80	S 0	11	22	9	S	Q	6
		174	175	180	188	214	215	231	232	258	275(M)
		50	œ	8	14	100	16	94	19	Э	27
(7)d .	m/e	39	4	43	4	45	46	51	52	53	58
	I(%)	100	31	94	21	31	40	27	4	21	21
		63	2	65	9 9	67	68	78	80	81	91
		15	15	4	35	17	13	21	15	19	13
		92	93	94	95	96	76	98	111	117	119
		13	21	38	60	4	42	31	æ	10	80
		120	121	122	123	136	137	138	139	140	141
		œ	31	6L	13	15	31	33	19	15	13
		173	174	175	189	190	214	215	216	231	232
		80	52	00	œ	œ	61	56	10	9	27
		233	234	235	277	278	279(M)				
		52	42	13	9	13	15				
(7)d,	a/m	39	6	4	45	46	51	52	53	8	94
	I(%)	52	28	16	16	81	13	16	19	6	27
		95	96	76	98	111	112	122	123	138	139
		85	100	25	36	16	12	65	16	38	30
		140	141	142	171	173	174	175	190	191	214
		11	7	11	7	7	38	9	6	9	s
		215	216	233	234	235	236	260	279	280(M)	
		83	13	13	56	33	7	ę	6	23	
(8)	a/m	41	42	43	4	45	59	69	70	71	83
	I(%)	14	30	7	69	\$	6	24	14	15	13
		84	85	86	100	110	111	126	127	128	154
		52	6	36	œ	53	10	Ś	100	10	7
		156	171(M)								
		4	e								

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8)d₄	m/e	39	8 (41	42	43 5	4 8	45	46	47	53
	I(%)	CS CS	77	\$	82	8/	37	78	100	7	٢
		Ł	55	56	57	58	61	62	67	88	69
		œ	6	7	6	9	90	6	7	13	74
		5	71	72	73	83	2 8	85	86	87	88
		56	23	29	34	7	26	67	50	28	4
		89	8	8	97	8	103	110	111	112	113
		65	16	13	œ	10	80	78	30	12	16
		114	128	129	130	131	156	159	160	174	175(M)
		6	24	77	33	10	4	7	15	1-5	5
(8)d ₅	m/e	42	43	4	45	4	62	63	2	69	70
	I(%)	33	34	¥	36	96	6	25	56	12	4
		11	72	73	85	86	87	88	68	8	67
		10	13	39	17	52	40	13	20	56	7
		100	<u>10</u>	107	108	111	112	113	114	129	130
		7	10	7	12	65	18	13	17	17	100
		131	132	133	157	160	161	175	176(M)		
		39	21	14	7	7	20	0-2	0-4		
į		:	:	!							
(6)	m/e	39	41	42	43	4	45	55	56	57	58
	I(%)	10	8	10	11	24	13	16	3	10	7 9
		59	69	70	73	82	83	85	86	67	98
		10	11	34	13	11	24	99	24	4	92
		8	100	110	114	125	127	138	139	153	154
		13	61	13	13	13	15	99	90	7	11
		155	156	170	171	182	199(M)				
		100	13	48	7	11	œ				
*p(6)	a/m	41	4	55	56	57	58	59	99	71	72
	I(%)	24	21	14	22	19	4	4	4	16	22
		75	86	87	88	68	97	98	8	<u>10</u>	101
		13	14	48	80	19	13	33	83	43	13
		102	103	110	117	127	130	138	139	156	157
		16	4	10	10	11	10	73	22	24	100
		158	173	174	175	184	203(M)				1
		32	Π	35	9	13	9				

(9)d.	m/e	41	42	43	4	45	4	56	57	58	59
\$ \$	I(%)	9	9	- 00	43	25	100	9	9	80	12
		8	70	72	73	28	86	87	88	89	8
		10	7	9	80	9	80	21	S	6	10
		98	66	<u>8</u>	101	102	103	104	105	106	107
		S	6	13	œ	S	6	12	4	80	15
		108	109	136	137	139	140	141	157	158	159
		28	5	5	4	œ	9	4	9	13	œ
		160	173	174	175	185	203	204(M)			
		5	9	17	20	1	2.4	3			
(10)	m/e	41	42	43	4	45	2	55	56	57	59
	1(%)	30	6	41	16	6	9	27	21	7	9
		67	68	69	70	72	62	81	82	83	84
	•	6	7	14	21	5	7	5	10	s.	s
		86	95	96	76	98	100	112	113	114	124
		14	Ś	6	12	S	10	6	9	21	6
		139	140	141	152	15 3	154	155	156	166	181
		9	9	27	6	\$	28	s	26	S	6
		183	209	210	226	227	250	267	268	311(M)	
		11	S	s	100	16	15	38	6	5	
7P(01)	m/e	41	42	43	4	45	4	2	55	56	57
•	I(%)	55	19	59	58	29	18	11	58	33	34
		58	67	6 8	69	70	11	72	73	81	82
		18	12	14	23	17	21	19	10	80	21
		83	84	88	68	95	96	76	8 6	8	102
		15	10	12	11	80	14	14	14	14	10
		103	112	113	114	115	116	124	125	139	140
		10	11	12	18	27	19	23	14	12	19
		141	142	143	152	153	154	155	156	157	158
		21	4	38	12	10	18	6	33	22	27
		159	160	210	211	227	228	229	230	231	232
		25	10	11	10	18	55	<u>0</u>	68	33	6
		250	151	252	267	268	269	270	271	272	295
		18	18	11	7	23	41	32	17	9	0-1
		296	313	314	315(M)	316					
		14	1.8	2.9	е. Е	7					

(10)d.	m/e	41	42	43	4	45	46	55	56	57	69
a	I(%)	14	Ş	18	6	9	œ	18	6	×	œ
		70	11	72	73	83	89	96	8	100	103
		Ś	9	10	œ	s	6	9	5	7	S
		104	113	114	115	116	117	124	140	141	142
		Q	Q	7	14	14	5	5	7	ය	16
		143	<u>4</u>	152	153	154	155	156	157	158	159
		37	9	ŝ	15	7	12	32	15	7	15
		160	165	167	168	169	170	183	184	185	186
		19	4	Ŷ	24	23	10	Ś	9	4	9
		187	210	211	228	229	230	231	232	251	252
		80	4	9	œ	37	2 8	100	15	17	6
		253	254	268	269	270	271	272	281	296	297
		4	4	S	20	45	21	œ	ŝ	9	7
		314	315	316(M)							
		2	4	s							
Coumarin	a/m	39	4	51	62	33	68	8	101	118	144
3-carboxamide	I(%)	11	11	9	œ	15	25	12	11	17	s
		145	146	161	173	174	189(M)	190			
		17	12	5	85	11	<u>10</u>	14			

Mass spectrometric studies-VII

m/e	Composition	
89	C ₇ H ₅	
90	C ₇ H ₆	
91	C_7H_7	
102	C ₈ H ₆	
103	C_8H_7	
106	C ₇ H ₈ N	
117	C ₈ H ₇ N	
129	C _o H _o O	
131	C ₆ H ₇ O	
145	C _o H ₇ NO	
146	C ₉ H ₈ NO	
102	C ₈ H ₆	- ·
103	C ₈ H ₇	
104	C ₇ H ₆ N	
105	(C ₇ H ₅ O	(18%)
	{C7H2N	(64%)
	lC₅H₀	(18%)
106	$C_{7}H_{8}N$	
131	C ₀ H ₇ O	
146	C _o H _a NO	
147	C ₄ H ₂ O ₂	
148	C.H.O.	(50%)
	C ₀ H ₁₀ NO	(50%)
189	C. HoNo	(/0)
190	C.,H.,N.O.	
193	C. H. N	
194	$C_{14}H_{11}N$	
252	$C_{16}H_{16}N_2O$	
44	{CH₂NO	(33%)
69	$\begin{cases} C_2 H_6 N \\ C_3 HO_2 \\ C_4 H O \end{cases}$	(00%) (28%) (72%)
70	C ₃ H₄NO	(63%)
	C_4H_8N	(37%)
71	$C_3H_7N_2$	
83	C₄H₅NO	
84	C₄H₅NO	
85	(C ₃ H ₅ N ₂ O	(32%)
	{C₄H ₇ NO	(28%)
	(C4H9N2	(40%)
86	∫C ₃ H₄NO ₂	(44%)
	}C₄H₅NO	(56%)
100	C ₄ H ₈ N ₂ O	
127	C ₆ H ₁₁ N ₂ O	
55	C ₄ H ₇	
56	C ₃ H ₆ N	
57	∫C ₃ H ₇ N	(59%)
)C₄H,	(41%)
58	C ₃ H ₈ N	
	m/e 89 90 91 102 103 106 117 129 131 145 146 102 103 104 105 106 131 146 147 148 189 190 193 194 252 44 69 70 71 83 84 85 86 100 127 55 56 57 58	m/e Composition 89 C_7H_5 90 C_7H_6 91 C_7H_7 102 C_8H_6 103 C_8H_7 106 C_7H_8N 117 C_8H_7N 129 C_9H_3O 131 C_9H_7O 145 C_9H_7NO 146 C_9H_8NO 102 C_8H_6 103 C_9H_7NO 146 C_9H_7NO 105 (C_7H_7N) C_8H_9 OO 104 C_7H_8N 131 $C_9H_7O_2$ 146 C_9H_8NO 147 $C_9H_7O_2$ 148 $\{C_9H_8O_2$ $\{C_9H_1ONO$ $\{B9$ $C_10H_9N_2O_2$ $[90$ $C_10H_9N_2O_2$ $[93$ C_14H_{11N} $[94$ $C_14H_{10}NO$ $[24H_6N$ 70 $(C_3H_4NO$ C_4H_8N C_1H_6NO 86

TABLE 2. ION COMPOSITION FROM HIGH RESOLUTION MEASUREMENTS

70	C₄H ₈ N	
83	C ₅ H ₇ O	
85	C ₄ H ₉ N ₂	
86	$C_3H_4NO_2$	
97	∫C₄H ₅ N ₂ O	(33%)
	C ₅ H ₇ NO	(66%)
98	∫C₅H ₈ NO	(91%)
	C ₆ H ₂ N	(9%)
99	C ₄ H ₇ N ₂ O	(35%)
	{C ₅ H ₉ NO	(50%)
	C ₅ H ₁₁ N ₂	(15%)
100	C ₅ H ₁₀ NO	
110	C ₆ H ₈ NO	
138	C ₈ H ₁₂ NO	

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