Mass Spectra of Some *N*-Methyl-*N*-formylhydrazones

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Though hydrazones are seldom found in nature, they are nevertheless known to have biological activity. Some of them are toxic and synthetic derivatives of hydrazines are frequently used as growth stimulators or growth regulators.[1]

N-Methyl-*N*-formylhydrazones constitute one of the few groups of natural hydrazones. They have been found in the mushroom *Gyromitra esculenta* Pers. Fr., false morel, and accordingly called gyromitrins.[2-4] The toxicity of fresh *Gyromitra esculenta* has been attributed to these *N*-methyl-*N*-formylhydrazones, eight of which (*i.e.*, compounds *2*–*7*, *9* and *12* (*cis* and *trans*) in Table 1) have been identified.[2-5]

N-Methyl-*N*-formylhydrazones are important not only because of their toxicity but because they or their precursors may play a role in the growth regulating system of the exceptionally fast growing mushroom fruit body.

N-Methyl-*N*-formylhydrazones may be present in other natural products in addition to mushrooms and in those products they can be most easily identified on the basis of their specific mass spectral fragmentation. In order to assist their identifications, a series of *N*-methyl-*N*-formylhydrazones were synthesized from those carbonyl compounds common in nature and the spectra were measured.

Results and discussion. In the compounds *1*–*15* where there is the possibility of McLafferty rearrangement (Fig. 1a), the prominent peak $m/e = 59$ is seen in the spectra. Other typical peaks in the spectra of *1*–*15* are at masses $m/e = M - 29$, $M - 58$ and $m/e = 85$ (Fig. 1c).

In the spectra of *6*–*11*, the prominent peak at $m/e = 100$ gradually increases as the aliphatic chain becomes longer. The fragment $m/e = 100$ can be explained as due to the rearrangement schematized in Fig. 1b. This rearrangement is in agreement with the observation of Kleipool *et al.*[6] and Djerassi *et al.*[7] Kleipool *et al.*[6] have found that pentanal and higher aldehyde 2,4-dinitrophenylhydrazones (DNP) display an intensive peak at $m/e = 224$, which they attribute to β-fission of the alkyl chain with the accompanying hydrogen rearrangement. Since butanal DNP does not exhibit an $m/e = 224$ peak, they assume that a hydrogen atom in the δ-position is required, which is transferred to the *p*-nitro group bearing a positive charge. In contrast to the latter Djerassi *et al.*[7] have detected with deuterium labeled DNP that the hydrogen atom at γ-position is rather abstracted in this rearrangement. It was found that a hydrogen atom from a methyl group cannot be abstracted in this process. This explains the failure to observe the peak at $m/e = 224$ in the spectra of butanal DNP and the peak at $m/e = 100$ in the spectrum of butanal *N*-methyl-*N*-formylhydrazone, respectively.

Analogously to the compounds *6*–*11*, the rearrangement (Fig. 1b) in the spectra of *19* and *20* yields the peaks at $m/e = 128$ and $m/e = 126$ (Fig. 1d). The peaks $m/e = 99$ and $m/e = 97$ can be attributed to the fragments $m/e = 128 - 29$ (CHO) and $m/e = 126 - 29$, respectively, and the peaks at masses $m/e = 71$ and $m/e = 69$ to the fragments $m/e = 99 - 28$ ($N{=}CH_2$) and $m/e = 97 - 28$, respectively.

In the spectra of the compounds *16*–*20*, prepared from ketones, there are prominent peaks at masses $m/e = M - R^1$ and $m/e = M - R^2$.

Experimental. Mass spectra were recorded with a Jeol JMS-D 100 mass spectrometer, connected to a gas chromatograph. The compounds were injected through a 50-m FFAP glass capillary column, programmed from 60 to 220 °C, 8 °C per min. Ionizing voltage was 75 eV, ionizing current 300 μA. The temperatures: injection block 200 °C, interphase oven 200 °C

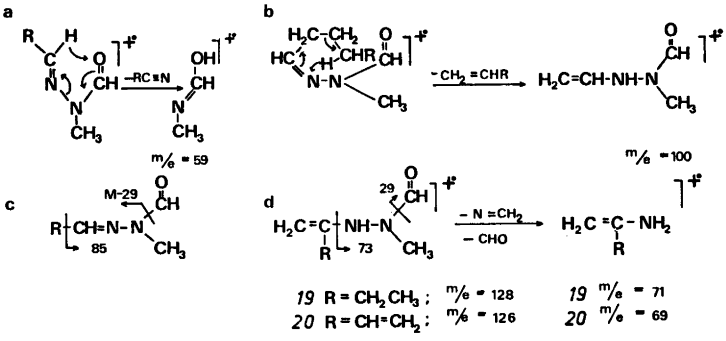
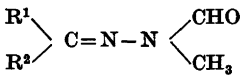


Fig. 1. Mass spectral fragmentation patterns of *N*-methyl-*N*-formylhydrazones.

Table 1. Mass spectra of *N*-methyl-*N*-formylhydrazones.



Compound	R^1	R^2	Mass spectrum
1	H	H	42(30), 43(100), 57(47), 59(100), 72(13), 86(33)
2	CH_3	H	42(60), 57(65), 59(100), 71(30), 85(25), 100(20)
3	C_2H_5	H	43(69), 56(94), 59(90), 71(25), 85(100), 99(3), 114(8)
4	C_3H_7	H	41(52), 43(60), 59(93), 60(85), 70(40), 73(30), 85(100), 128(12)
5	$(CH_3)_2CHCH_2$	H	41(56), 43(80), 57(28), 59(100), 60(19), 71(31), 84(54), 85(89), 100(10), 127(9), 142(13)
6	C_4H_9	H	41(34), 43(50), 57(25), 59(73), 60(19), 67(8), 69(21), 71(25), 84(39), 85(100), 100(48), 113(8), 142(16)
7	C_5H_{11}	H	43(68), 55(25), 59(78), 60(41), 71(20), 85(100), 98(54), 100(57), 113(10), 127(3), 156(12)
8	C_6H_{13}	H	40(88), 43(100), 44(100), 59(85), 71(26), 85(90), 100(78), 113(55), 141(3), 170(15)
9	C_7H_{15}	H	41(60), 43(100), 59(90), 60(43), 69(20), 71(18), 85(78), 100(60), 113(8), 126(28), 155(2), 184(1)
10	C_8H_{17}	H	41(90), 59(75), 60(63), 85(95), 100(100), 114(10), 140(38), 169(5), 198(17)
11	C_9H_{19}	H	41(55), 43(91), 59(60), 60(55), 83(30), 85(90), 100(100), 113(15), 154(40), 212(13)
12	$CH_3(CH_2)_4CH=CH$ (*trans*)	H	41(60), 43(38), 55(37), 59(100), 70(17), 73(27), 124(53), 139(10), 153(6), 182(15)
13	C_4H_3O (furyl)	H	39(93), 43(57), 52(91), 53(82), 59(100), 81(55), 94(55), 95(55), 123(52), 152(25)
14	C_6H_5	H	51(55), 59(75), 77(63), 89(38), 90(41), 104(100), 118(18), 133(30), 162(25)
15	$C_6H_5CH_2$	H	43(18), 51(20), 65(20), 77(16), 85(100), 91(40), 103(10), 117(8), 142(6), 147(5), 176(3)
16	CH_3	CH_3	44(17), 56(38), 71(7), 85(10), 99(100), 114(37)
17	C_2H_5	CH_3	41(39), 42(100), 43(75), 57(30), 59(88), 68(15), 86(25), 99(98), 113(12), 128(17)
18	C_3H_7	CH_3	41(100), 43(100), 56(58), 73(30), 84(15), 99(100), 127(50), 142(35)
19	C_5H_{11}	C_2H_5	43(92), 55(52), 71(63), 73(90), 99(20), 113(100), 128(20), 141(10), 155(67), 184(10)
20	C_5H_{11}	$CH_2=CH$	43(95), 55(47), 60(35), 69(100), 73(87), 83(34), 97(25), 111(80), 124(15), 126(8), 139(20), 153(30), 182(8)

and the ion source 220 °C.

The *N*-methyl-*N*-formylhydrazones were synthesized from *N*-methyl-*N*-formylhydrazine and the carbonyl compounds analogously to the method described by List *et al.*,[2] and the ^1H NMR and IR spectra were in accordance with the proposed structures.

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Received June 14, 1976.