

Short Communications

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OXIDATION OF 2-(4-HYDROXYPHENYL)-3-METHYLINDOLE WITH HYDROGEN PEROXIDE

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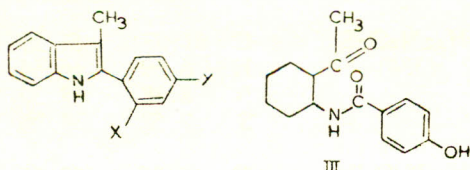
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The autooxidation of 2-(2-hydroxyphenyl)-3-methylindole (I) to yield 3-hydroxy-2-(2-hydroxyphenyl)-3-methyl-3H-indole has already been reported [1-3]. It was also found [1] that 2-(4-hydroxyphenyl)-3-methylindole (II) under the same conditions does not undergo autooxidation. Reaction of compound (II) with hydrogen peroxide has now been studied and it has been found that hydrogen peroxide cleaves the indolic 2,3-bond and affords *N*-(2-acetophenyl-4-hydroxybenzamide) (III). The structure of (III) was supported by its IR spectrum which in particular showed the presence of two carbonyl functions (1655 and 1640 cm^{-1}), and by its mass spectrum which showed *m/e* at 255.



when $x = -\text{OH}$, $-\text{H}$; $y = -\text{H}$, $-\text{OH}$ respectively

EXPERIMENTAL

M. ps. were recorded on a Kofler hot stage apparatus, UV spectrum in ethanolic solution (95%) on a Perkin-Elmer model 137 spectrophotometer, IR in nujol on a Perkin-Elmer model 237 spectrophotometer, and mass spectrum with an A.E.I. MS-12 spectrometer. Solutions, were dried over anhydrous magnesium sulphate and evaporations were carried out under reduced pressure (water pump). Solid analytical sample was dried over phosphorus pentoxide at 80°/0.1 mm for 4 hr.

N-(2-Acetophenyl-4-hydroxybenzamide) (III)

2-(4-Hydroxyphenyl)-3-methylindole(II) [1] (0.50 g) was added to hydrogen peroxide solution (6%, 25 ml) and the mixture heated on a steam bath for 12 hr. The white crystalline solid (0.49 g, 89%) was separated by filtration and recrystallised from benzene

to afford *N*-(2-acetophenyl-4-hydroxybenzamide)(III) as white needles m.p. 214-215° (0.24 g, 44%). (Found C, 70.8; H, 5.0; N 5.3; *m/e*, 255. $\text{C}_{15}\text{H}_{13}\text{NO}_3$ requires: C, 70.8; H, 5.1; N, 5.5%; mol wt. 255) λ_{max} 218, 248 and 341 nm ($\log \epsilon = 4.48, 4.37$ and 4.03); λ_{infel} 279 nm ($\log \epsilon = 4.04$); ν_{max} 3330, 3180 (NH;OH), 1655 and 1640 cm^{-1} (CO,NHCO).

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MASS SPECTRAL STUDIES ON DIMORPHOLINOETHANE

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Gero [1] was the first to synthesise dimorpholinoethane (DME) by the reaction of 1,2-dibromoethane with morpholine. Ali *et al.* [2,3] studied the complexes of DME with transition metal halides, followed up by Vekappayya *et al.* [4] and Lott *et al.* [5-7] who carried out further research on DME metal complexes. The analytical aspects of DME for gravimetric estimation of a number of metal ions have been looked into by Asmus *et al.* [8-13]. The use of DME in some industrial processes is also known [14]. Recently, Hussain *et al.* [15] have carried out a comparative study of the magnetic, spectroscopic and conductance properties of DME and dimorpholinopropane [DMP] metal complexes.

In the present communication the mass spectrum of the ligand dimorpholinoethane, not reported earlier, is described and discussed.

As in our earlier investigations [5], in the present study also, DME was prepared in the laboratory by the method of Gero. The elemental analyses of the product were not done as these have already been reported [15]. Samples for mass spectral study were further purified by recrystallization from anhydrous-methanol. The traces of solvent methanol were removed by drying the samples in a desiccator over anhydrous calcium chloride for long enough period. The mass spectrum was obtained in VG-Micromass 12 mass spectrometer.

The detailed mass spectrum of dimorpholinoethane (Fig. 1) indicated a very low intensity mass peak at *m/e* 200 corresponding to the molecular ion ($\text{C}_{10}\text{H}_{20}\text{O}_2\text{N}_2$)⁺. The very low intensity of this parent molecular ion is obviously due to its greater ins-

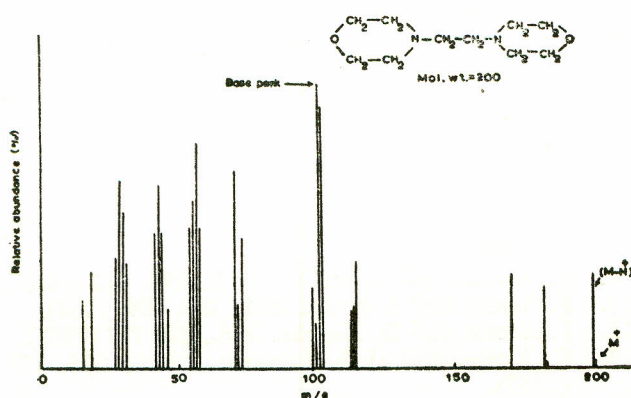


Fig. 1. Mass spectrum of dimorpholinoethane. (DME).

tability. The mass spectrum did not show any mass peak at m/e value higher than 200, confirming the molecular weight of the ligand to be 200. The fragmentation of the molecular ion appeared to start with the elimination of neutral fragment H as indicated by a reasonably intense mass peak at m/e 199 (33.71%) corresponding to (M-H) molecular ion ($C_{10}H_{19}O_2N_2$)⁺. Since chain branching is more favourable point of cleavage [16], the elimination of neutral fragment H could possibly be from either of the two branched $CH_2-CH_2-O-CH_2-N$ -entities and not from the straight chain (CH_2-CH_2).

From a study of the mass spectrum (Table 1) the most probable mechanistic pathway for the fragmentation process of dimorpholinoethane is postulated as follows:

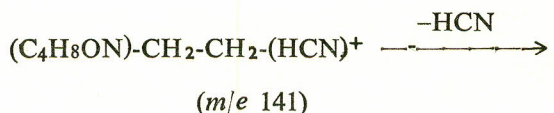
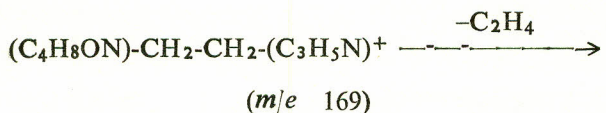
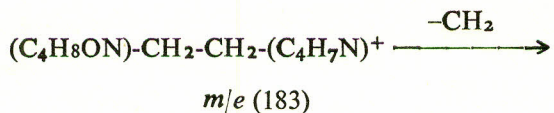
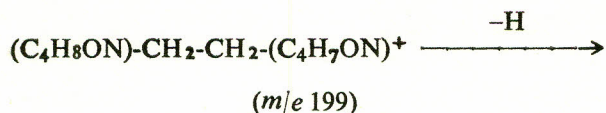
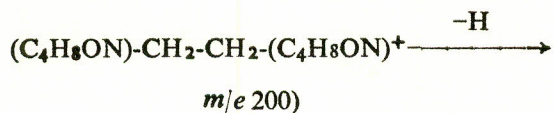
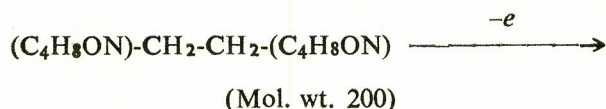
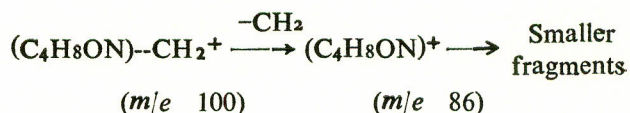
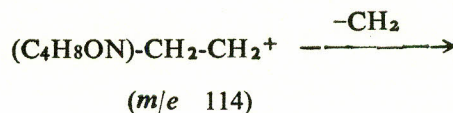


Table 1. Mass Spectrum of dimorpholinoethane (DME)

m/e	Abundance %	m/e	Abundance %	m/e	Abundance %
14	6.86	53	5.57	97	3.99
15	24.57	54	49.71	98	29.71
16	6.57	55	60.57	99	15.99
17	17.99	56	80.57	100	100
18	35.14	57	50.86	101	91.43
26	21.71	58	18.57	102	10.28
27	39.99	63	3.43	111	3.43
28	66.86	67	2.86	112	20.86
29	55.43	68	13.99	113	22.28
30	36.57	69	16.57	114	38.86
31	19.43	70	66.86	115	3.99
32	15.25	71	22.28	141	3.71
39	12.29	72	46.28	149	3.14
40	7.71	77	3.43	169	8.86
41	47.99	81	4.57	170	34.86
42	65.71	82	12.86	171	4.28
43	48.57	83	11.71	182	29.43
44	33.99	84	18.57	183	3.43
45	20.57	85	12.57	199	33.71
51	3.43	86	6.57	200	3.43
52	3.71	87	4.57		

Only % abundance greater than 3 are reported.
 m/e value smaller than 14 are not given.



Further fragmentation of the morpholine molecular ion (C_4H_8ON)⁺ can take place through more than one pathways forming smaller fragments as $C_2H_4^+$, H_2O^+ , HCN^+ , CH_2^+ and CO^+ . Mass peaks at m/e value corresponding to these molecular ions have been observed in the mass spectrum (Table 1). The maximum intensity of mass peak at m/e 100 corresponding to the fragment ion (C_4H_8ON)- CH_2^+ indicates its greater stability and the very high possibility of the formation of this fragment ion during the fragmentation process of DME. The intense mass peaks at m/e 182, and m/e 170 are due to molecular ion (C_4H_8ON)- $CH_2-CH_2-(C_4H_6N)^+$ and (C_4H_8ON)- $CH_2-CH_2-(C_3H_6N)^+$, formed respectively due to

the elimination of fragments H and C from the molecular ion, $(C_4H_8ON)-CH_2-CH_2-(C_4H_7N)^+$ formed at m/e 183. The intense mass peaks at m/e 101 (91.43%) and m/e 70 (66.86%) could be due to the fragment ions $(C_5H_{11}ON)$ and $(C_4H_8)^+$ respectively.

The mass spectrum did not show any metastable peak.

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