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Mass spectral studies of nitroindole compounds

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ABSTRACT

5-Nitro-2-aryl-1H-indole-3-carboxaldehydes have been synthesized by new improved and green chemistry techniques. Final confirmation is achieved from Fast atomic bombardment (FAB) mass spectra which exhibit molecular ion peak (M^{+1}) of compounds corresponding to their molecular masses. The fragmentation pathways of 5-nitro-2-(4-bromophenyl)-1H-indole-3-carboxaldehyde and 5-nitro-2-(4-fluorophenyl)-1H-indole-3-carboxaldehyde have been discussed. These spectra show some preferential fragmentation pattern.

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KEYWORDS

5-Nitro-2-aryl-1H-indole-3-carboxaldehydes;
Green chemistry techniques;
Fast atomic bombardment;
Molecular ion peak;
Fragmentation pattern.

INTRODUCTION

Heterocyclic chemistry is one of the largest branches of chemistry. Indole moiety has been reported as a common denominator of heterocyclic compounds exhibiting psycho-tropism spectrum of biological activities^[1-5].

Mass spectra of some indole derivatives have been discussed earlier^[6-10] but The mass fragmentation pattern of 5-Nitro-2-aryl-1H-indole-3-carboxaldehydes has not been reported earlier in literature. So keeping these things in mind, we have investigated the fragmentation pathways of some nitro indole derivatives.

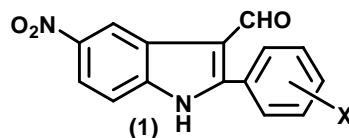
EXPERIMENTAL

A new green protocol was developed to synthesize the 5-nitro-2-aryl-1H-indole-3-carboxaldehydes (**1a-i**)^[11].

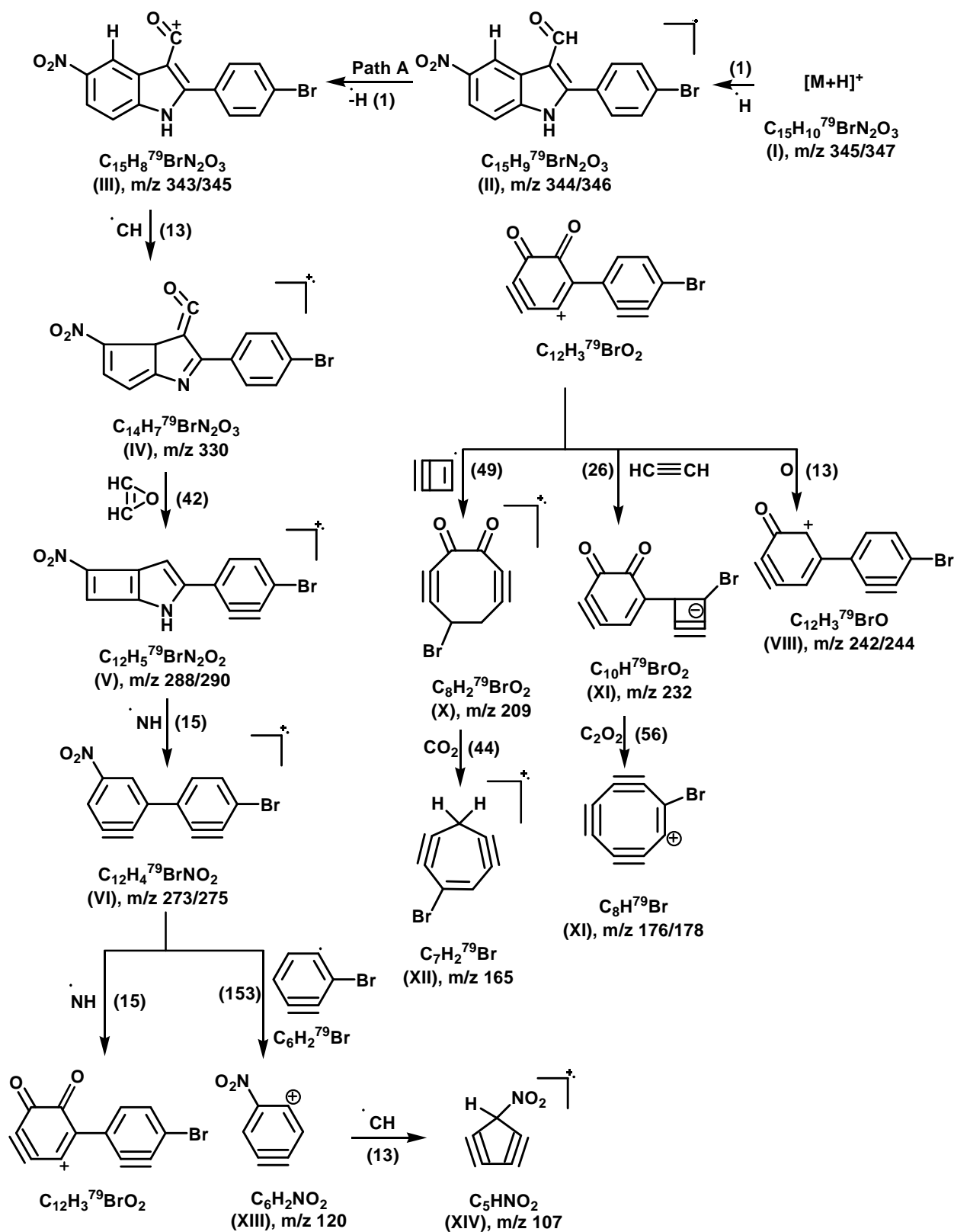
The mass spectra were recorded on Jeol SX-102 FAB mass spectrometer. FAB mass Spectral data of

5-nitro-2-aryl-1H-indole-3-carboxaldehydes (**1a-i**) have been tabulated in TABLE 2.

The mass fragmentation of compound (**1b**) and (**1d**) is discussed in detail. Compound (**1b**) (Scheme 1) under FAB provides a characteristic molecular ion cluster at m/z 345/347 (M^{+1}) (**I**) (38.84/37.6%). Cation (**I**) eliminates one hydrogen radical to give a cation radical **II** at m/z 344/346 **II** (100%, base peak) due to the presence of one bromine atom. This may fragment by one pathway A. In the pathway A, (**II**) eliminates a hydrogen radical to generate a cation (**III**) at m/z 343/345 (38.46/38.84%). Cation (**III**) by loss of CH radical gives cation radical (**IV**) at m/z 330 (15.38%). Cation radical (**IV**) eliminates C_2H_2O to give cation radical (**V**) at m/z 288/290 (7.69/7.07%). Cation radical (**V**) extruded neutral NH moiety to give a cation radical (**VI**) at m/z 273/275 (23.07/23.38%). This cation radical

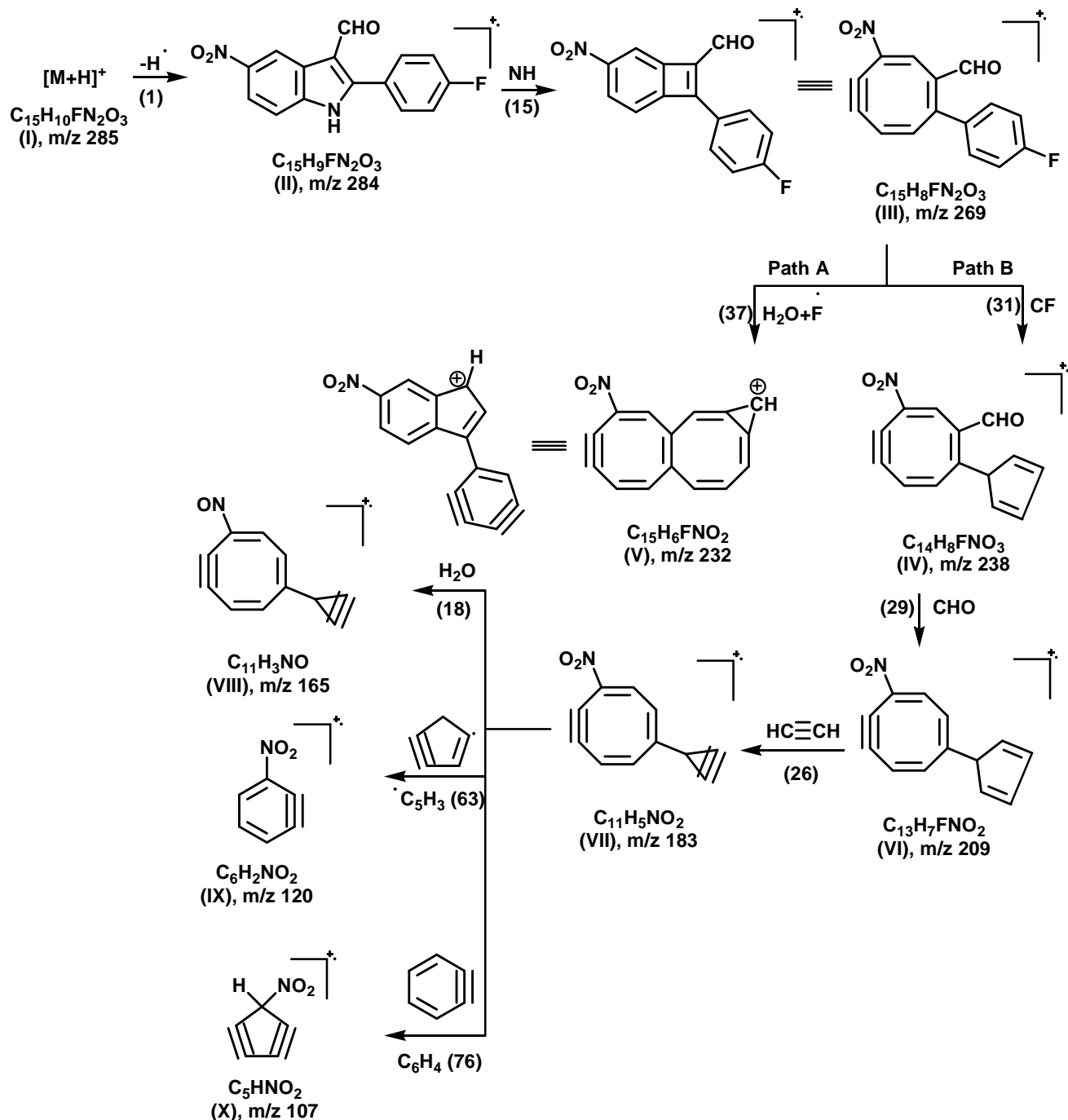


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Scheme 1: Mass fragmentation pattern of 5-nitro-2-(4-bromophenyl)-1H-indole-3-carboxaldehyde (1b)

(VI) further fragmented into two pathways. In first pathway it eliminates NH radical to afford cation (VII) at m/z 258 (15.38%). In second pathway, cation radical (VI) eliminates C_6H_2Br radical to afford cation (XIII)



Scheme 2 : Mass fragmentation pattern of 5-nitro-2-(4-fluorophenyl)-1H-indole-3-carboxaldehyde (**1d**)

at m/z 120 (46.15%) which in turn eliminates CH radical to give cation radical (**XIV**) at m/z 107 (92.30%). The cation (**VII**) in turn further decomposes in three possible pathways. In the first pathway cation (**VII**) loses neutral O atom to give cation (**VIII**) at m/z 242/244 (15.38/15.30%). In second pathway, it produces cation (**IX**) at m/z 232 (15.38%) by loss of neutral acetylene moiety which further eliminates C_2O_2 moiety to yield cation (**XI**) at m/z 176/178 (15.38/15.39%). In

third pathway, it loses C_4H radical undergoes ring expansions giving rise to the expanded eight-membered cyclo-octaditriene type cation radical (**X**) at m/z 209 (15.38%). Cation radical (**X**) further eliminates neutral CO_2 moiety to afford cation radical (**XII**) at m/z 165 (30.76%).

The mass fragmentation of compound (**1d**) is also discussed in detail. Compound (**1d**) (Scheme 2) under FAB provides a characteristic molecular ion peak at m/z

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TABLE 1 : FAB mass Spectral data of 5-nitro-2-aryl-1H-indole-3-carboxaldehydes (1a-i)

Compd. No.	X	MS (FAB) m/z (M ⁺ + 1)
1a	H	267
1b	4-Br	345/347*
1c	4-Cl	301 / 303*
1d	4-F	285
1e	3-NO ₂	312
1f	3-Cl, 4-F	319
1g	2-Cl, 4-F	319
1h	2-F, 5-Cl	319
1i	2-F, 5-CH ₃	299

* Due to isotopic cluster

TABLE 2 :Major mass fragments of 5-nitro-2-aryl-1H-indole-3-carboxaldehydes (1b & 1d)

Compd. No.	1b		1d	
Fragment No.	m/z	Relative intensity (%)	m/z	Relative intensity (%)
I	345/347 (M ⁺ +1)	38.84/37.60	285 (M ⁺ +1)	100
II	344/346 (M ⁺)	100	284	38.88
III	343/345	38.46/38.84	269	11.11
IV	330	15.38	238	16.66
V	288/290	7.69/7.07	232	8.33
VI	273/275	23.07/23.38	209	5.55
VII	258	15.38	183	2.77
VIII	242/244	15.38/15.30	165	5.55
IX	232	15.38	120	8.33
X	209	15.38	107	19.44
XI	176/178	15.38/15.39	-	-
XII	165	30.76	-	-
XIII	120	46.15	-	-
XIV	107	92.30	-	-

z 285 (M⁺+1) (**I**) (100%, base peak). The loss of a hydrogen radical from this peak afforded cation radical (**II**) at m/z 284 (38.88%). Cation radical (**II**) by loss of neutral NH moiety and undergoes ring expansion to yield eight membered cation radical (**III**) at m/z 269 (11.11%). Cation radical (**III**) fragmented by two pathways A and B. In the pathway A, (**III**) eliminates neutral water molecule and fluorin radical to generate a cation (**V**) at m/z 232 (8.33%). In the pathway B, cation radical (**III**) eliminates neutral CF and generates cation radical (**IV**) at m/z 238 (16.66%). Cation radical (**IV**) by loss of CHO group give cation radical (**VI**)

at m/z 209 (5.55%). Cation radical (**VI**) extruded neutral acetylene moiety to give cation radical (**VII**) at m/z 183 (2.77%). Cation radical (**VII**) further fragments by three possible pathways. In the first pathway, it eliminates neutral water molecule to yield cation radical (**VIII**) at m/z 165 (5.55%); In second pathway, it produces cation (**IX**) at m/z 120 (8.33%) by the loss of C₅H₃ radical. In third pathway, cation radical (**VII**) loses C₆H₄ neutral moiety giving rise to the cation radical (**X**) at m/z 107 (19.44%).

Major mass fragments along with their relative intensities and m/z values of (**1b**) & (**1d**) are tabulated in TABLE 1.

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