Mass Spectral Fragmentation Patterns of 2,3-Diphenylindole Derivatives and Dibenzo[*ac*]carbazoles

Rosa Erra-Balsells

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Pabellón 2,
3° Ciudad Universitaria,
1428 - Buenos Aires, Argentina

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The electron impact mass spectra of a variety of substituted 2,3-diphenylindoles have been examined and the major fragmentation routes ascertained. The mass spectra of several dibenzo[*ac*]carbazoles are also discussed. All of the results allow us to assume that 2,3-diphenylindoles would not cyclize in the spectrometer upon electron impact.

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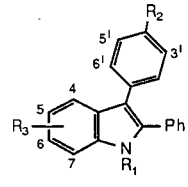
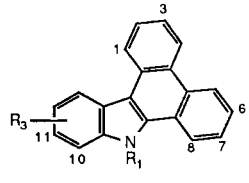
Very few reports describing the behavior of indole derivatives on electron impact appear in the literature. Beynon has described the spectra of eleven alkylindoles [1,2] and Powers has described the spectra, among others, of 1-, 2- and 3-phenyl and 2,3-diphenylindoles [3].

Our interest in thermal [4] and photochemical [5,6] reactions of 2,3-diphenylindole and its derivatives prompted us to compare their photoreactivity [5,6] with the behavior of the corresponding radical cations formed in the spectrometer. As it was reported by our laboratory [5] 2,3-diphenylindoles, under uv irradiation, produce a dehydrocyclization with formation of dibenzo[*ac*]carbazoles. Timmons [7] has correlated the effect of electronic impact and the effect of uv irradiation on stilbene compounds and he found that "if photocyclization takes place then cyclodehydrogenation must also occur on electrom impact to give a cyclized ion of relative abundance greater than 5%". In spite of the mass spectra of the indole derivatives (Scheme 1, Compounds **1**, **3**, **5**, **7**, **9**, **11** and **13**) show the presence of the M-1 and the M-2 ion with relative abundance greater than 5% (Table I), the difference observed in the mass spectra of the 2,3-diphenylindoles (Table I) and the corresponding dibenzocarbazoles (Table III) allow us to assume that the M-2 radical cation formed from indole molecules would be different than the $M^{+\cdot}$ obtained from dibenzocarbazoles because their mass spectral fragmentation patterns are different.

Scheme 1





	R_1	R_2	R_3
1	H	H	H
3	H	H	5 - Me
5	H	H	6 - Me
7	H	H	7 - Me
9	H	H	4,7 - diMe
11	Me	H	H
13	Ph	H	H
15	H	H	6 - NO_2
16	H	NO_2	H
17	H	NO_2	6 - Me
18	H	H	5 - NO_2
			6 - Me
19	H	NO_2	5 - NO_2
			6 - Me
20	H	NO_2	5 - Me
			6 - NO_2

	R_1	R_3
2	H	H
4	H	12 - Me
6	H	11 - Me
8	H	10 - Me
10	H	10,13 - diMe
12	Me	H
14	Ph	H

Table I

Relative Abundance of Principal Fragments for Compounds **1**, **3**, **5**, **7**, **9**, **11** and **13**
(Figures in parentheses correlate with those in Scheme 2)

Compound	M	M-1 (1)	M-2 (2)	M-3 (3)	M-R_1	M-Ph (4)	M-R_3 (5)	M-R_1NCPh (6)	M-R_1NCPh-R_3 (7)
1	100	55	61	5	55	—	55	10	—
3	100	25	8	10	25	7	28	10	10
5	100	55	15	20	55	12	38	21	14
7	100	22	13	10	22	12	38	8	15
9	100	22	4	6	22	8	18 5 (M-2Me)	7	10
11	100	9	3	2	12	2	4	2	—
13	100	99	98	98	70	70	99	40	18

Scheme 2

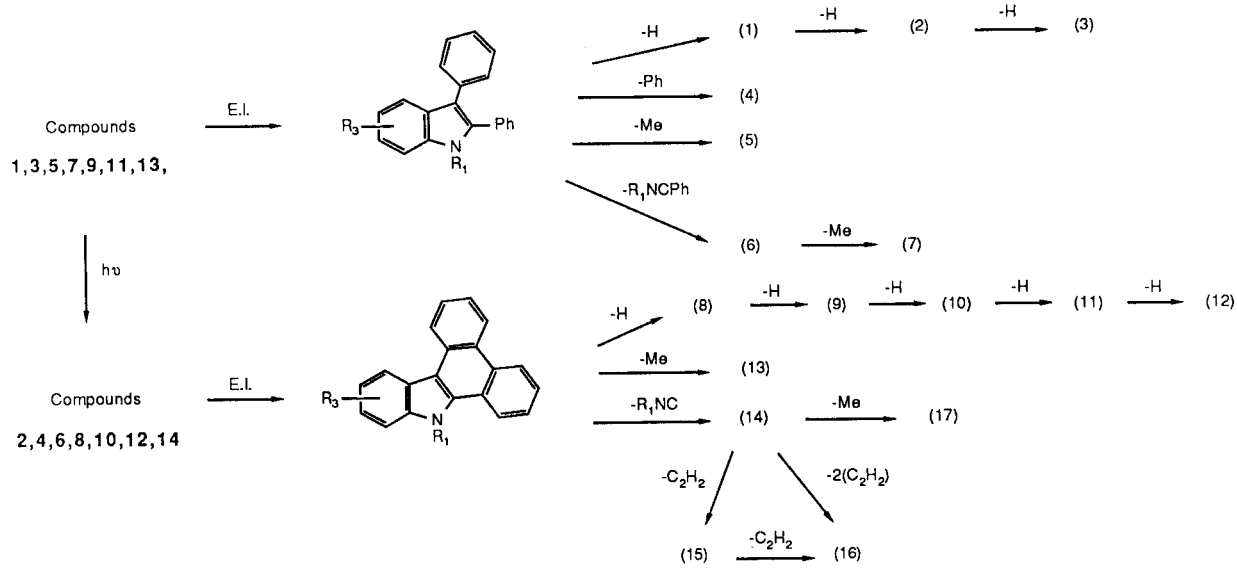


Table II

Relative Abundance of Principal Fragments for Compounds **15-20**

Compound	M	M-Me	M-Ph	M-Ph -Me	M-HO	M-NO	M-NO_2	M-NO_2 -1	M-NO_2 -2	M-NO_2 -Me	M-NO_2 -Ph	M-NO_2 -HNC	M-R_2- HNCPh	M-R_2- HNCPh-R_3	M-HNCPh- R_3
15	100	—	60	—	—	49	85	63	32	—	65	10	—	—	8
16	52	—	7	—	—	2	100	45	50	—	3	7	18	4	3
17	99	10	—	12	—	14	100	84	4	99	10	77	71	81	4
18	100	12	5	8	76	—	88	32	48	6	4	9	—	—	65 (R_3 = NO_2) 3 (R_3 = Me)
19	100	18	—	40	75	—	22	10	4	11	8	7	4	9 (R_3 = NO_2) 7 (R_3 = Me)	4 (R_3 = NO_2) 5 (R_3 = Me)
20	100	22	—	61	88	4	30	13	7	15	10	13	3	5 (R_3 = NO_2) 7 (R_3 = Me)	8 (R_3 = NO_2) 14 (R_3 = Me)

Table III

Relative Abundance of Principal Fragments for Compounds **2**, **4**, **6**, **8**, **10**, **12** and **14**
(Figures in parentheses correlate with those in Scheme 2)

Compound No.	M	M-1 (8)	M-2 (9)	M-3 (10)	M-4 (11)	M-5 (12)	M-R (13)	M-R_1NC (14)	M-R_1NC-C_2H_2 (15)	M-R_1NC-$(C_2H_2)_2$ (16)	M-R_1NC-Me (17)	141, 140, 139.
2	100	51	64	74	49	37	—	70	50	5	—	—
4	100	63	80	57	76	9	75 ($R = R_3$)	89	6	8	11	77, 100, 78
6	100	78	54	77	53	67	74	38	11	6	37	72, 66, 60
8	100	81	53	66	49	52	69	41	10	11	43	75, 49, 75
10	100	11	71	40	12	—	72	19	2	—	2	12, 71, 66
12	71	66	75	6	12	—	88 ($R = R_1$)	66	—	—	—	100, 59, 11
14	95	100	62	94	78	56	59	70	—	—	—	—

For the compounds formulated in Scheme 1 the relative abundances of the ions are compiled in Tables I-III. The most important fragmentation pathways for the compounds compiled in Tables I and III are shown in Scheme 2 and the probable fragmentation patterns are discussed below.

I - Fragmentation Pattern of 2,3-Diphenylindoles **1**, **3**, **5**, **7**, **9**, **11** and **13** (Schemes 1, 2, Table I).

The major cleavage of these compounds upon electron impact may be plausibly interpreted as follows: All compounds are very stable under electron impact due to their heteroaromaticity which favors the molecular ion to be observed as the base peak. In all cases the M-1 and the M-2 ions are very important. The question then arises whether it is necessary to represent the M-2 ion of 2,3-diphenylindole as dibenzo[*ac*]carbazolenium ion rather than as simple unrearranged indolenium ion. The difference observed in the mass spectra of each 2,3-diphenylindole-dibenzo[*ac*]carbazole pair allow us to assume that the cyclization would not take place in the spectrometer. In contrast to that which was described for phenylindoles [3], from the unrearranged 2,3-diphenylindolenium ions the loss of HCN, H_2CN and H_3CN are not the predominant fragmentation pathway. Only compounds **1** and **13** show the loss of R_1CN from $M^{+\cdot}$ (Relative abundance 3 and 4% respectively). In contrast the ($M-R_1NC$) ions are always present in the mass spectra of the corresponding dibenzo-[*ac*]carbazoles (Table III) being very important peaks.

The phenyl (Ph) and R_1NCPh groups are lost in the well-known manner [3] from molecular indole ions giving predominant fragments in these spectra (Table I). Besides, when R_1 = Ph (**13**, Scheme 1) the ($M-R_1NC$) ion (45%) is also observed indicating the lack of scrambling in this fragmentation pathway. Loss of Ph and R_1NCPh group is not detected in the mass spectrum of the corresponding dibenzo[*ac*]carbazoles (Table III and Scheme 2). These results would suggest that a retro-electrocyclic reaction from dibenzo[*ac*]carbazoles do not take place in the spectrometer upon electron impact.

On the other hand, loss of the Me radical occurs as readily from **3**, **5**, **7**, **9** (R_3 = Me) and **11** (R_1 = Me) (Table I) as from **4**, **6**, **8**, **10** (R_3 = Me) and **12** (R_1 = Me) (Table III). The formation of (M-Me) ion would suggest that a common intermediate (M-1) azaazulenium ion, in analogy with the formation of quinolinium ion from 2-methylindoles, is not formed. Both intermediates have been previously proposed, the former to explain the spectra of 4-, 5-, 6- and 7-methylindole [1-3] and the latter to explain the spectra of 2-methylindole derivatives [1-3 and 8].

II - Fragmentation Pattern of Nitro-2,3-diphenylindoles **15-20** (Scheme 1, Table II).

As it can be seen in Table I, the predominant peaks in the spectra of 2,3-diphenylindoles are the M and M-1 peaks. Introduction of a nitro group into the 5 or the 6 position or into the *para* position of the 3-phenyl substituent (R_2 = NO_2, Scheme 1) results in the disappearance of the (M-1) and (M-HNCPh) ions from the spectra of these compounds (Table II). These effects could be due to destabilization of the M-1 ion by the nitro group being this substituent preferentially directing the fragmentation of the molecule. After loss of the nitro group, which is supported by the presence of the corresponding metastable ion in the spectra of compounds **15**, **16** and **18-20** (relative abundance 1; 0.7; 1.8 and 2% respectively), the major fragmentation routes (see Table II, ($M-NO_2$)-1, ($M-NO_2$)-2, ($M-NO_2$)-Me, ($M-NO_2$)-HNCPh, ($M-NO_2$)-HNCPh-R_3) from ($M-NO_2$) ion are similar to those previously described in Scheme 2 and in Table I.

On the other hand, loss of HO radicals only occurs from compounds **18**, **19** and **20** (see Scheme 1) *o*-isomers in which a six-membered transition state would account for the formation of (M-HO) fragment [9], indicating the lack of scrambling in this fragmentation pathway.

III - Fragmentation Pattern of Dibenzo[*ac*]carbazoles (Schemes 1 and 2, Table III).

Some aspects of the mass spectral fragmentation patterns of dibenzo[*ac*]carbazoles have been discussed in section I.

The mass spectrum of **2** reveals that phenanthrenium (m/e 178) and florenium (m/e 166) ion [10] are not formed from the molecular ion. In addition, we compared this spectrum with those of phenanthrene and fluorene (see both mass spectra in Experimental) and no correlation was observed.

The major cleavages of these compounds upon electron impact may be plausibly interpreted by typical fragmentation pathways of heterocyclic aromatic compounds (loss of HNC, R_1NC and C_2H_2 [9]).

As expected the peaks of m/e 139, 140 and 141 are pronounced peaks in all spectra of methyldibenzo[*ac*]carbazoles (**4**, **6**, **8**, **10** and **12**) being a good evidence of the formation of a common ion, probably a methylquinolinium ion ($C_{10}H_7N$, $C_{10}H_6N$ or $C_{10}H_5N$).

Consistent with the behavior of indole compounds which localize the charge in the indolic portion of the molecule rather than in another group both series of compounds, 2,3-diphenylindoles (Tables I and II) and dibenzo-[*ac*]carbazoles (Table III) undergo fragmentation to yield ions of m/e 133 and 134 (relative abundance 8-90%). The mass spectrum of 9*H*-dibenzo[*ac*]carbazole (**2**) and its methyl derivatives (**4**, **6**, **8**, **10** and **12**) show peaks at m/e 120 and 121 (5-20%).

In the mass spectrum of all the examples studied (**1-20**) the ions of m/e 77, 65, 63 and 51 (7-23%) were detected.

In conclusion, compounds **1-20** give characteristic frag-

ments with high intensities under electron impact (Tables I-III). Besides, neither 2,3-diphenylindole derivatives studied would dehydrocyclize to dibenzo[*ac*]carbazoles nor dibenzo[*ac*]carbazoles [11] would give a retro-electrocyclic reaction upon electorn impact (Scheme 2).

EXPERIMENTAL

The mass spectra were recorded on a MS-Varian Mat CH-7A/Data System 166 at 15 and 70 eV. Data listed in Tables I-III were obtained at 70 eV. The samples were introduced by a direct inlet probe and were heated at 200°. Compound purity was checked by tlc and mp.

Compounds **1-20** (Scheme 1) have been prepared by methods described by us [4,5]. Their melting points, elemental analyses, uv and pmr spectra have been previously reported [4,5].

Phenanthrene (Aldrich Chemical Co.) was recrystallized from 95% ethanol and had mp 100-101° (lit [12] mp 99-101°); ms: (m/e) 178 (M, 82), 177 (95), 176 (66), 175 (63), 174 (88), 163 (13), 153 (68), 152 (72), 151 (100), 150 (76), 139 (63), 128 (58), 127 (45), 126 (81), 125 (11), 115 (9), 102 (11), 89 (78), 88 (70), 77 (62), 76 (93), 75 (60), 63 (43).

Fluorene (Aldrich Chemical Co.) was recrystallized from benzene-ethanol and had mp 113-115° (lit [12] mp 116-117°); ms: (m/e) 166 (M, 100), 165 (80), 164 (54), 163 (66), 139 (13), 115 (8), 89 (5), 84 (5), 83 (13), 63 (6).

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[10] An ion of m/e 164 (78%) was observed in the mass spectrum of **14**.

[11] Dibenzo[*ac*]carbazoles were recovered unchanged after uv irradiation in acetic acid or in dichloromethane solution. These irradiations were performed according to methods previously described by us (acetic acid solution [5] and dichloromethane solution [12]).

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