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SYNTHESES AND MASS SPECTRAL STUDIES OF SOME BENZDIAZOLES AND N-SKATYLTRIAZOLE

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Syntheses of *N*-skatylbenzimidazole (I), *N*-skatyl-2-methylbenzimidazole (II), *N*-skatyl-2-benzylbenzimidazole (III), *N*-skatyl-1,2,3-benzotriazole (IV) and β-(*N*-benzimidazolyl)-ethyl 3-phenanthryl ketone (V) have been achieved through alkylation reaction of gramine. Their mass spectra have been studied by analysing metastable peaks and mass numbers.

In earlier communications we have described some alkylation reactions of Mannich bases.[1,2,3,4] In the present communication gramine and β-morpholinoethyl 3-phenanthryl ketone hydrochloride have been utilized as alkylating reagents for the syntheses of the corresponding *N*-substituted benzimidazoles and a triazole, viz. *N*-skatyltriazole, for detailed mass spectral studies on the electron impact fragmentation of these types of compounds.

Gramine reacts with benzimidazole, 2-methylbenzimidazole, 2-benzylbenzimidazole, and 1,2,3-benzotriazole in aqueous medium to give the corresponding *N*-substituted benzdiazoles and *N*-triazole when refluxed. Similarly, benzimidazole reacts with β-morpholinoethyl 3-phenanthryl ketone hydrochloride to give the corresponding β-(*N*-benzimidazoyl)-ethyl 3-phenanthryl ketone.

The mass spectrum (Fig. 1) of *N*-skatylbenzimidazole (I) showed a molecular ion peak at m/e 247^+ (24%; a). This ion underwent fragmentation to loose benzimidazole moiety to give a very stable charged skatyl species at m/e 130^+ (100%; m*57; base peak). The molecular ion (a) also lost CH_2N to give rise to (b) at m/e 219^+ (15%; m* 193.5). Yet a further fragmentation of (a) took place in the form of the loss of C_9H_7N with the transfer of one of its γ-protons to yield the benzimidazole ion (c) at m/e 118^+ (45%; m* 56.4). The ion (c) gave rise to charged species at m/e 77^+ (27%; m* 49.1; phenyl) and m/e 76^+ (21%; m* 49; phenonium ion). The other significant fragmentation ions were at m/e 208^+ (5%); 194^+ (27%); 128^+ (5%) 126^+ (7%) and 102^+ (19%).

The mass spectrum (Fig. 2) of *N*-skatyl-2-methylbenzimidazole (II) showed an intense molecular ion peak at m/e 261^+ (95%). This molecular ion underwent further fragmentation to give very stable species of skatyl at m/e 130^+ (100%; m* 66; base peak) as was observed in the previous case. The loss of one proton from this species gave rise to charged indolenine at m/e 129^+ (30%). This molecular ion also lost the skatyl moiety ($-C_9H_7N$) with the migration of a γ-proton to form the 2-methylbenzimidazole molecular ion species m/e 132^+ (78%; m* 66.7). Loss of the methyl group from the molecular ion also occurred to yield an ion at m/e 246^+ (12%). This loss of methyl group also took place from the ion m/e 132^+ to form an ionic moiety at m/e 117^+ (10%) followed by the metastable peak at m* 103. This charged ion again underwent further fragmentation to give charged phenyl and phenonium ions at m/e 77^+ (27%) and 76^+ (22%) respectively. The other important peaks were at m/e 245^+, 233^+, 219^+, 190^+, 165^+, 164^+, 143^+, 133^+, 131^+, 103^+ and 102^+. The general fragmentation pattern of its mass spectrum is outlined in Chart 2.

The mass spectrum (Fig. 3) of *N*-skatyl-2-benzylbenzimidazole (III) gave a significant molecular ion at m/e 337^+ which again gave rise to a similar stable charged skatyl moiety due to the cleavage of carbon and nitrogen bond at m/e

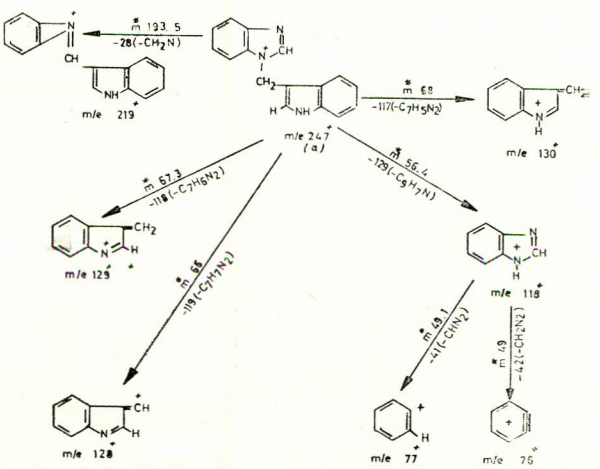

Chart 1.—Mass fragmentation pattern of *N*-skatylbenzimidazole.

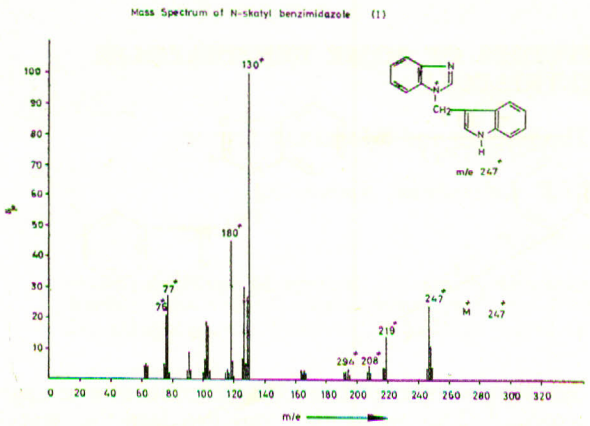

Fig. 1.—Mass spectrum of *N*-skatylbenzimidazole.

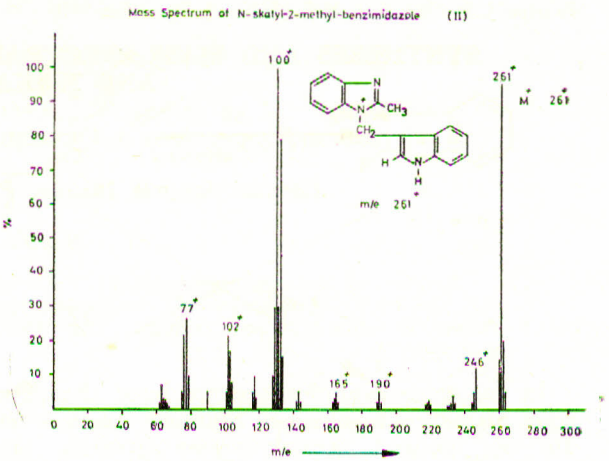

Fig. 2.—Mass spectrum of *N*-skatyl-2-methylbenzimidazole.

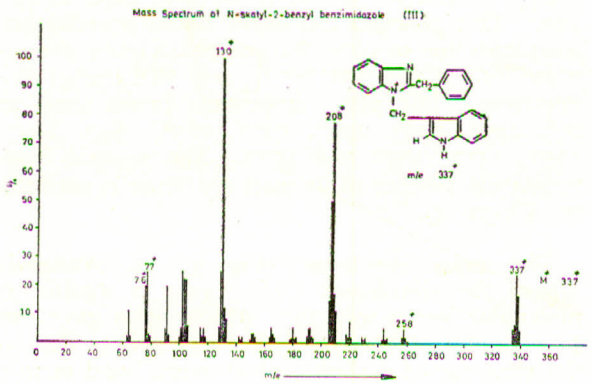

Fig. 3.—Mass spectrum of *N*-skatyl-2-benzylbenzimidazole.

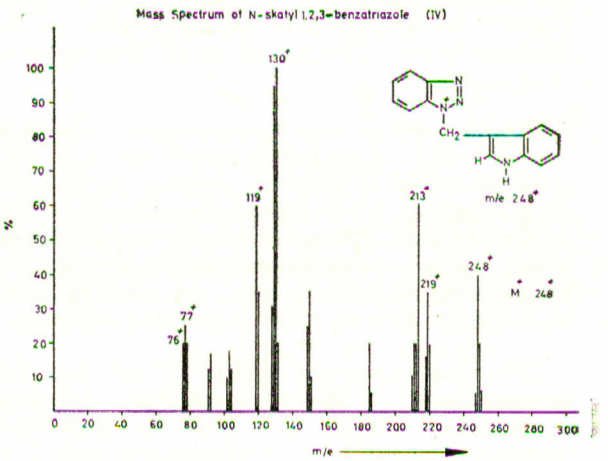

Fig. 4.—Mass spectrum of *N*-skatyl-1,2, 3-benzatriazole.

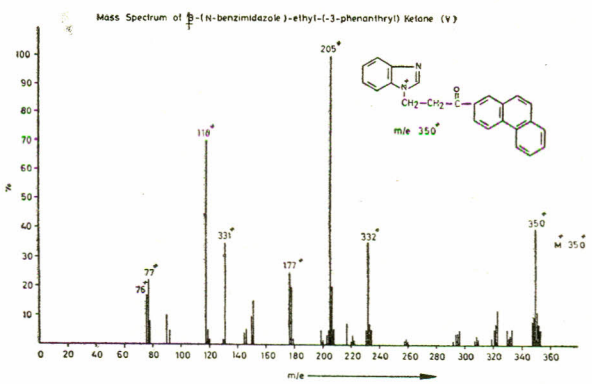

Fig. 5.—Mass spectrum of β-*N*-(benzimidazole)-ethyl 3-phenanthryl ketone.

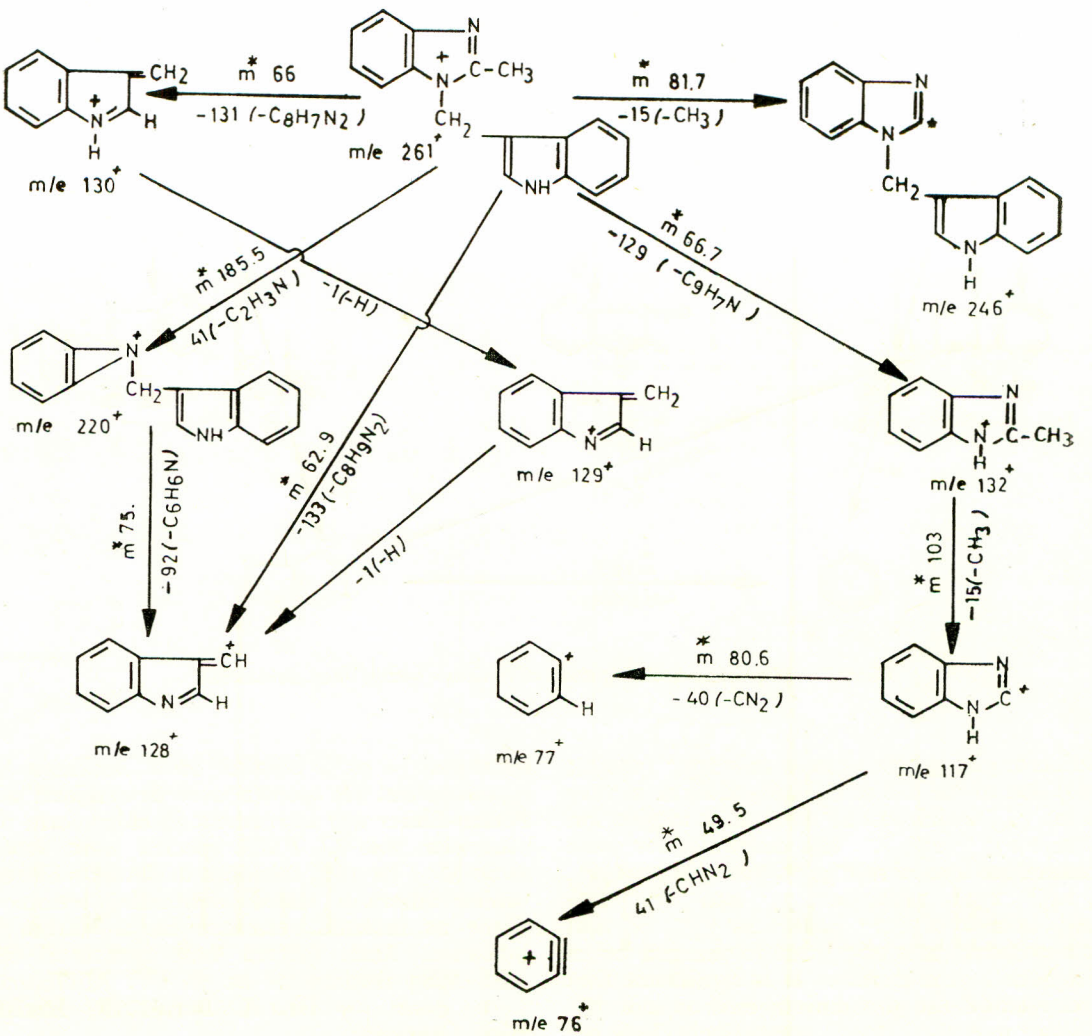

Chart 2.—Mass fragmentation pattern of *N*-skatyl-2-methylbenzimidazole.

130+ (100%; m* 50; base peak). It again formed an indolenine ion at m/e 129+ (25%). The loss of the skatyl moiety with the migration of one proton formed a significant benzylimidazole ion at m/e 208+ (75%; m* 128.9). The benzylimidazole ion (m/e 208+) underwent fragmentation to give rise to a peak at m/e 117+ (5%; m* 65.5) which on further fragmentation gave rise to phenyl and phenonium ions at m/e 77+ (25%) and m/e 76+ (20%) respectively followed by their appropriate metastable peaks.

The mass spectrum (Fig. 4) of *N*-skatyl-1,2,3-benzotriazole (IV) gave a significant molecular ion peak at m/e 248+ (40%) which afforded the skatyl ion at m/e 130+ (100%; m* 67.5; base peak) on further fragmentation, as was noticed in all the three previous cases. A charged species (d) at m/e 219+ (35%; m* 193) was formed due to the loss of 29 mass units from the molecular ion. This further fragmented to a stable species (e) at m/e 103+. Triazole ion, formed due to the rupture of carbon and nitrogen bonds with migration of one proton, appeared at m/e 119+ (66%; m* 57.5). The phenyl and phenonium ions as usual appeared with the same percentage ratios of 25 and 20 at m/e 77+ and m/e 76+ as recorded in the previous three spectra.

The mass spectrum (Fig. 5) β-(*N*-imidazoyl)-ethyl 3-phenanthryl ketone (V) showed molecular ion at m/e 350+ (40%). This underwent frag-

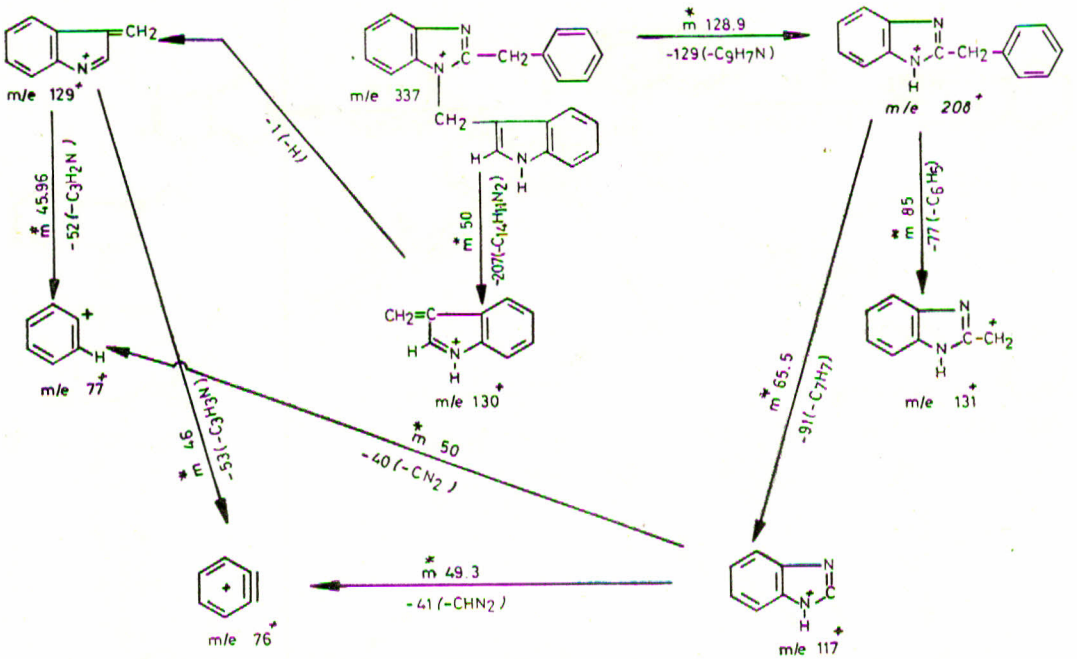

Chart 3.—Mass fragmentation pattern of *N*-skatyl-2-benzyl-benzimidazole.

mentation to give a base peak at m/e 205^+ (100%; m* 120) due to the loss of $C_9H_9N_2$ to form a very stable ion (f) which lost 28 mass units to give ion (g) at m/e 177^+ (25%). The molecular ion peak gave numerous ions at m/e 323^+, 322^+, 217^+, 146^+, 146^+, 145^+, 131^+, 118^+, 90^+, 77^+ and 76^+. The intensity of m/e of 131^+ peak was 35% of that of the base peak (m/e 205^+) due to charged ion of *N*-methylenebenzimidazole. It is significant that the phenyl and the phenonium ions at m/e 77^+ (22%) and m/e 76% (17%) respectively show the same difference of 5% in their percentage intensities as observed in all previous cases. It is interesting to know that when there is no skatyl substituent on the benzimidazole as in all the previous cases, the base peak does not appear at m/e 130^+.

The mass spectra of the above compounds reveal that whenever skatyl group is attached to imidazole or triazole, the base peak in their mass spectra appears at m/e 130^+ due to the skatyl moiety and independent of the nature of other substitutents in the molecule.

Experimental

Melting points were taken on a Kofler block, and are uncorrected. Light petroleum refers to the fraction b.p. 65–85°. UV spectra were measured in 95% ethanol on a Beckman DK-2 spectrometer. IR spectra were determined with a Perkin-Elmer 237 instrument in chloroform unless otherwise stated. PMR spectra were recorded at 60 Mc/s for 12% solutions in deuterochloroform (unless otherwise stated) containing tetramethylsilane as internal reference on a Varian A60 machine. Mass spectra were measured on an AEI MS9 instrument at 70 eV. Microanalyses were done by Dr. A. Bernhardt, Mullheim, West Germany.

N-*Skatylbenzimidazole* (*I*).—A mixture of gramine (0.52 g, 0.003 mole) and benzimidazole (0.59 g, 0.005 mole) was taken up in distilled water (50 ml) and refluxed (7.5 hr). The slightly pink crystalline solid obtained was filtered off, dried at room temperature and crystallized from hot methanol. N-*skatylbenzimidazole* was obtained in colourless needles, m.p. 206–7°C (0.7 g, 92.2%). λ_{max} 234 mμ (ε 9274), 277.5 mμ (ε 1614) and 285 mμ (ε 9274); $\nu_{max.}$ at 3130 NH), 2915, 2830 (—CH_2—; *asym* and *sym* stretching) 1605, 1579 (phenyl); 1350, 1285 (C—N stretching); 760, 735 cm^{-1} (*ortho* disubstitution on benzene). Other bands at 1490, 1450, 1380, 1365, 1247, 1265, 1193, 1100 and 1005 cm^{-1}. (Found: C, 78.52; H, 5.29; N, 16.93. $C_{16}H_{13}N_3$ requires: C, 77.71; N, 5.30 N, 16.99%).

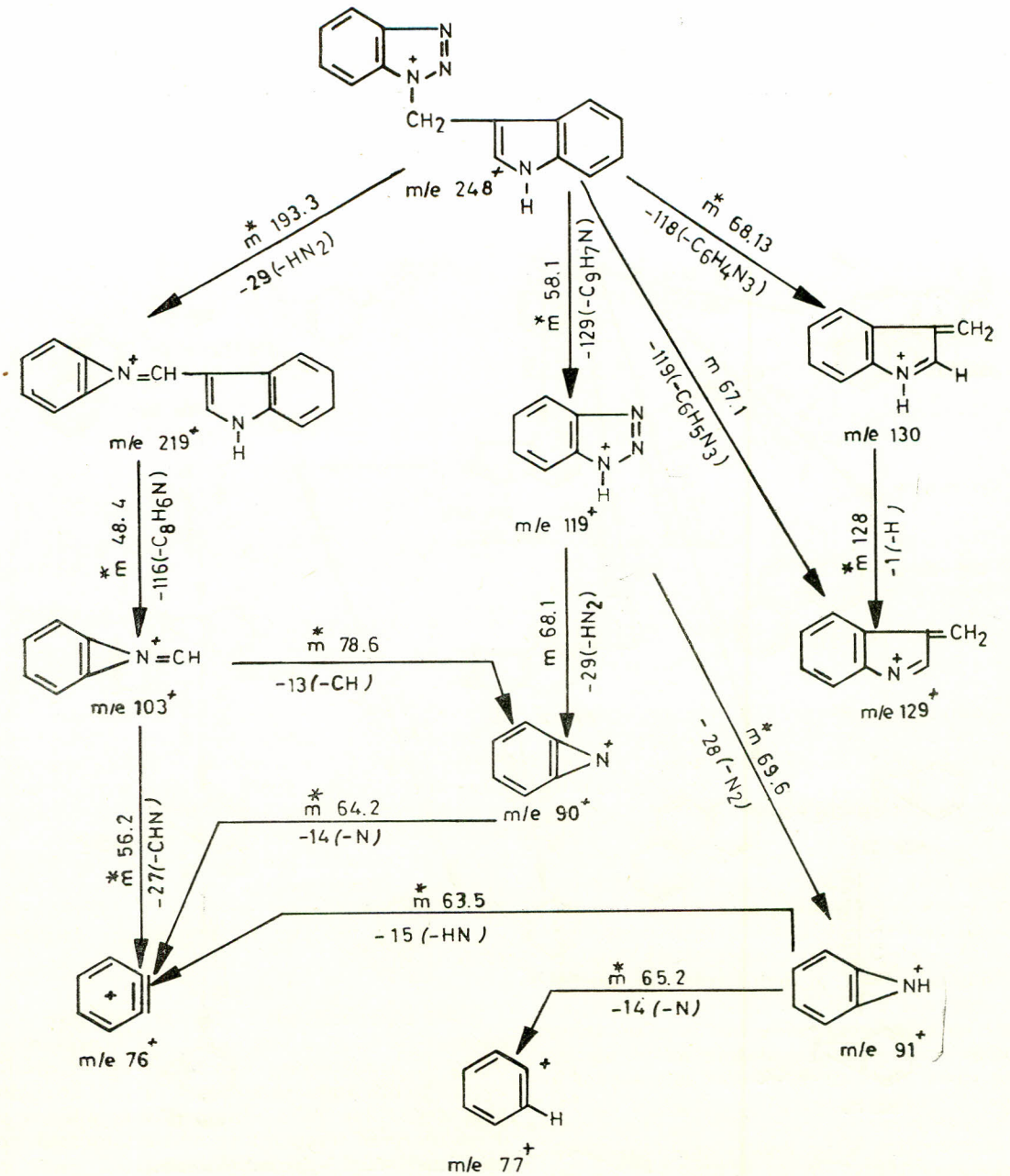

Chart 4.—Mass fragmentation pattern of *N*-skatyl-1, 2, 3-benzo-triazole.

PMR spectrum showed a singlet at τ5.5 (1H on the α-position of the pyrole ring) and another singlet appeared at τ 4.8 (1H-; N—C*H*—N). There was sharp singlet at τ4.4 (2H; —CH_2—). It also showed a multiplet at τ 2.82 (8H; benzenoid protons).

N-Skatyl-2-Methylbenzimidazole (*II*).—A mixture of gramine (0.52 g; 0.003 mole) and 2-methylbenzimidazole (0.53 g; 0.004 mole) was taken up in distilled water (50 ml) and heated on a sand bath (7 hr). The slightly pink crystalline solid obtained was filtered off, dried at room

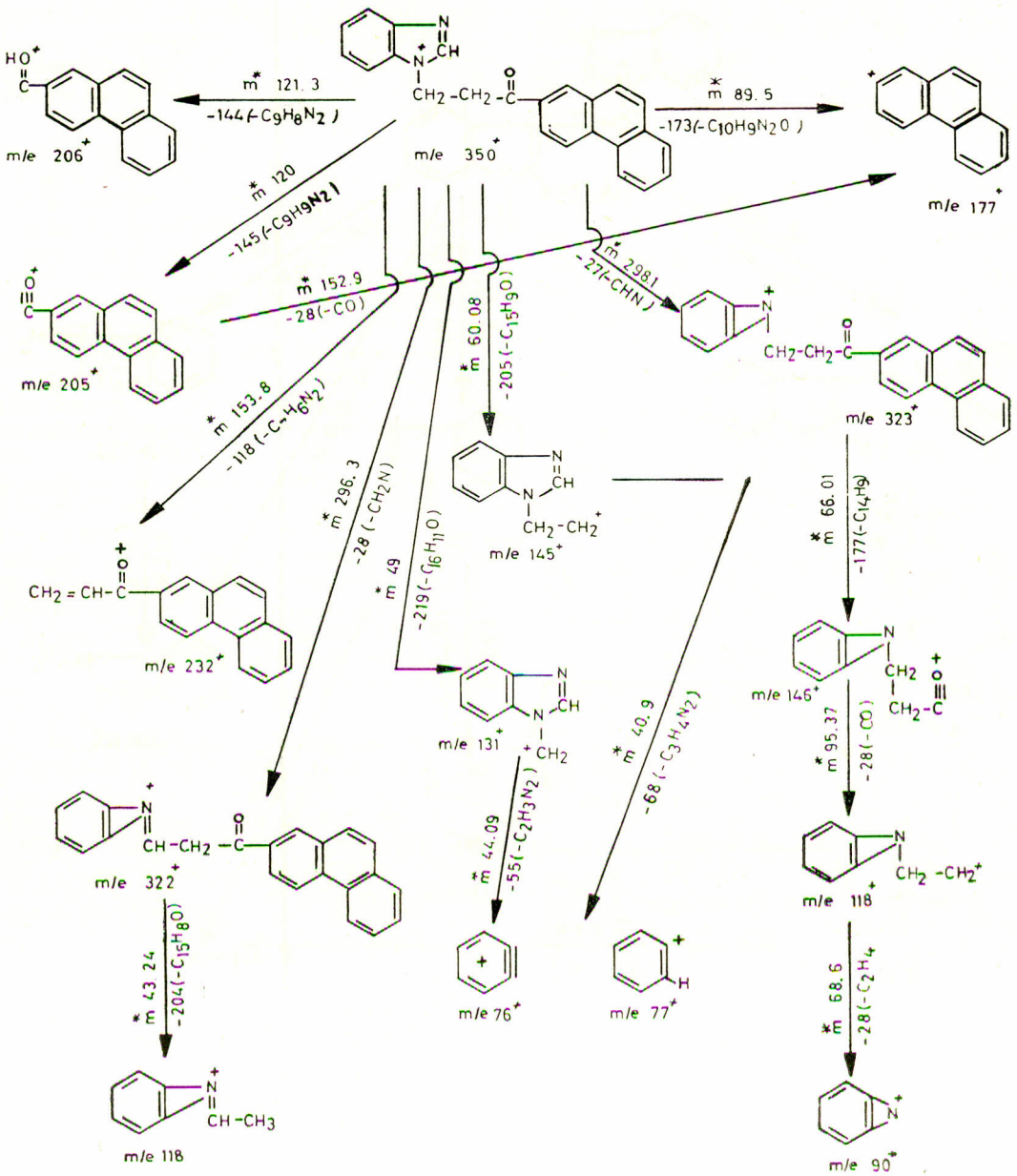

Chart 5.—Mass fragmentation pattern of β-(*N*-benimidazolyl)-ethyl 3-phenanthryl ketone.

temperature and crystallized from ethanol. *N-skatyl-2-methylbenzimidazole* was obtained in very slightly pink prismatic needles (m.p. 203–4°C clear melt, 0.72g, 92.3%).

It is moderately soluble in acetone, methanol, ethanol, chloroform, propylene glycol, dioxane and aqueous acetic acid (10%) but insoluble in water, benzene, ethyl acetate, ether, petroleum ether and carbon tetrachloride. λ_{max} 288.5 mμ (ε 1199), 282 mμ (ε 1629), 274 mμ (ε 681), shoulder at 267 mμ (ε 1896), 253.5 mμ (ε 5049). ν_{max} at 3100 cm^{-1} (>NH), two bands at 1580 and 1615 cm^{-1} (benzene stretching). (Found: C, 78.71; H, 5.80; N, 16.00. $C_{17}H_{15}N_3$ requires: C, 78.13; H, 5.79; N, 16.08%).

Its PMR spectrum (in pyridine d_6) showed a sharp singlet at τ 7.37 (3H; N—C—C*H*$_3$); a sharp singlet at τ 4.4 (2H, N—C*H*$_2$—C); a broad multiplet centred at τ 2.73, (8H; benzenoid protons). A hump appeared at τ 5.13 (1H; —N*H* which disappeared on deuteration) and a singlet at 2.54 (1H; C—N*H*—).

N-*Skatyl-2-Benzylbenzimidazole* (*III*).—A mixture of gramine (0.52 g, 0.003 mole) and 2-benzylbenzimidazole (0.64 g, 0.003 mole) was taken up in distilled water and refluxed (7 hr). The slightly pink solid obtained was filtered off, dried at room temperature. Ethanol gave colourless prismatic needles of N-*skatyl-2-benzylbenzimidazole* (m.p. 196–197°C clear melt, 0.97g, 95.3%).

It is soluble in dioxane, moderately in acetone, ethanol, methanol and propylene glycol and insoluble in water, benzene, ethyl acetate, aqueous acetic acid (10%), ether, petroleum ether and carbon tetrachloride. λ_{max} at 287 mμ (ε 7305), 280 mμ (ε 1132), 260 mμ (ε 1132) and 234.5 mμ (ε 8865); ν_{max} at 3100 cm^{-1} (>NH) and 1580, 1610 cm^{-1} (benzene stretching). (Found: C, 82.46; H, 5.42; N, 12.8. $C_{23}H_{19}N_3$ requires: C, 81.87; H, 5.68; N, 12.45%).

The PMR spectrum (pyridine d_6) showed a singlet at τ 5.5 (2H; —C*H*$_2$—); a singlet at τ 4.4 (2H; N—C*H*$_2$—), a multiplet centred at τ 2.75 (13H; all protons on the benzene rings, a hump at τ 5.15 (1H; C—C*H*—NH—) and a multiplet at τ 1.95 (1H, C—N*H*—C).

N-*Skatyltriazole* (*IV*).—A mixture of gramine (0.52 g, 0.003 mole) and benztriazole (0.59g, 0.003 mole) was refluxed (1.5 hr) in water (50 ml). Filtration under reduced pressure gave N-*skatyltriazole* which crystallised from ethyl acetate (colourless needles, m.p. 241°C clear melt, 0.6g, 80.9%).

N-Skatyltriazole is soluble in acetone, methanol, ethanol, benzene, dioxane and insoluble in water, petroleum ether, chloroform and carbontetrachloride. λ_{max} 275 mμ (ε 73733), 255 mμ (ε 49333) and 220 mμ (ε 173600); ν_{max} (Nujol) 3279 cm^{-1} (NH), 1618 and 1597 cm^{-1} (benzene stretching). (Found: C, 72.2; H, 4.7; N, 22.6. $C_{15}H_{12}N_4$ requires: C, 72.5; H, 4.8; N, 22.5%.)

The PMR spectrum (DMSO) showed a singlet at τ 6.58 (2H; N—C*H*$_2$—C), multiplets between τ 2.5 and 3.2 (8H; benzene protons), a doublet at τ 2.34 (1H; J 2 c/s; —N—CH—C and a hump at τ 1.4 (1H; N*H*) which collapsed on addition of D_2O.

β-(N-*Benzimidazoyl*)-*ethyl 3-phenanthryl ketone* (*V*).—A mixture of β-morpholinoethyl 3-phenanthryl ketone hydrochloride (0.72 g, 0.002 mole), and benzimidazole (0.71 g, 0.006 mole) was taken up in distilled water (50 ml) and heated on sand bath (10 hr). The slightly yellow solid so obtained was filtered off and dried in air. β-(N-*benzimidazoyl*)-*ethyl 3-phenanthryl ketone* (*V*) crystallised from acetic acid, m.p. 177–8°C (clear melt); 0.72 g (quantitative). It is soluble in acetone, chloroform, ethyl acetate, methanol, propylene glycol and dioxane; moderately in ethanol and methanol and insoluble in distilled water, ether, petroleum ether and carbon tetrachloride. λ_{max} (in chloroform) 295 mμ (ε 881100), 281 mμ (ε 18580) shoulder at 260 mμ (ε 88270). ν_{max} (Nujol) 3080 cm^{-1} (NH), 1665 cm^{-1} (C—O) 1600 cm^{-1} and 1585 cm^{-1} (benzene stretching). (Found: C, 82.08; H, 5.06; O, 5.20; N, 7.78. $C_{24}H_{18}N_2O$ requires: C, 82.26; H, 5.18; O, 4.57; N, 8.00%).

The PMR spectrum ($CDCl_3$) showed a triplet centred at τ 6.15 (2H: A_2B_2 system; J_{AB} 7 c/s: —N—CH$_2$—C*H*$_2$—C—O), a triplet centred at τ 5.20 (2H; A_2B_2 system; J_{AB} 7 c/s: N—C*H*$_2$—CH$_2$—C) multiplets in the region τ 2–2.8, 13H; all benzenoid protons) and a singlet at τ1.8 (1H; N—C*H*—N).

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