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DIBORANE AS A REDUCING AGENT - VI

THE NOVEL REDUCTION OF INDOLE-1-CARBOXALDEHYDES TO 1-METHYL-INDOLES, DI(INDOLYLMETHYL)ETHERS AND INDOLYLMETHYL INDOLINES[1]

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Abstract - Reduction of the indole-1-carboxaldehydes (1a - 1f) with borane/THF gives the 1-methylindoles (4) in 42-91% yields together with the di(indolylmethyl)ethers (8), the indolylmethyl indolines (7), the unsymmetric ether (10) and the indolenine (11) as the minor products, except 7a. This appears to be the first report on the formation of symmetric ethers in the borane/THF reduction of an oxygen function. The formation of 7a and 7b from 1a and 1b implies that electrophilic substitution takes place primarily at position 3 of 3-substituted indoles. 1c - 1f did not form the corresponding 7 probably because of steric hindrance. These results are discussed in relation to the mechanisms of borane/THF reduction, origin of the different products and electrophilic substitution in 3-substituted indoles.

Reduction of indole-1-ketones with borane complexes or other reducing agents is not always successful and not well established.[2-9] Earlier, we reported for the first time the successful reduction of indole-1-carboxaldehydes, i.e. 1g and 1h, with borane/THF.[10] Since our results were limited and not sufficient to draw any firm conclusion,[10] and since no further work in this area seems to have appeared in the literature, and since indole-1-carboxaldehydes cannot be reduced with any other reagents,[10,11] we considered it worthwhile to carry out the reduction of additional indole-1-carboxaldehydes with borane/THF to study the generality, scope and limitations of the reaction, as well as, to throw further light on the mechanisms of both borane/THF reduction and electrophilic substitution in 3-substituted indoles, particularly because there exist some records in the literature in favour of direct electrophilic substitution at position 2 of the latter.[12]

Six indole-1-carboxaldehydes (1a - 1f) were reduced with excess borane/THF, and in each case, more than one product was obtained, the 1-methylindoles (4) being the major product, except in the case of 1a which gave the dimer (7a) in slightly greater proportion (Table 1). A related dimer (7b) was also obtained from 1b as the minor product. The new class of symmetric ethers (8b, 8d - 8f), the unsymmetric ether (10) and the indolenine (11) were also obtained as the other minor products.

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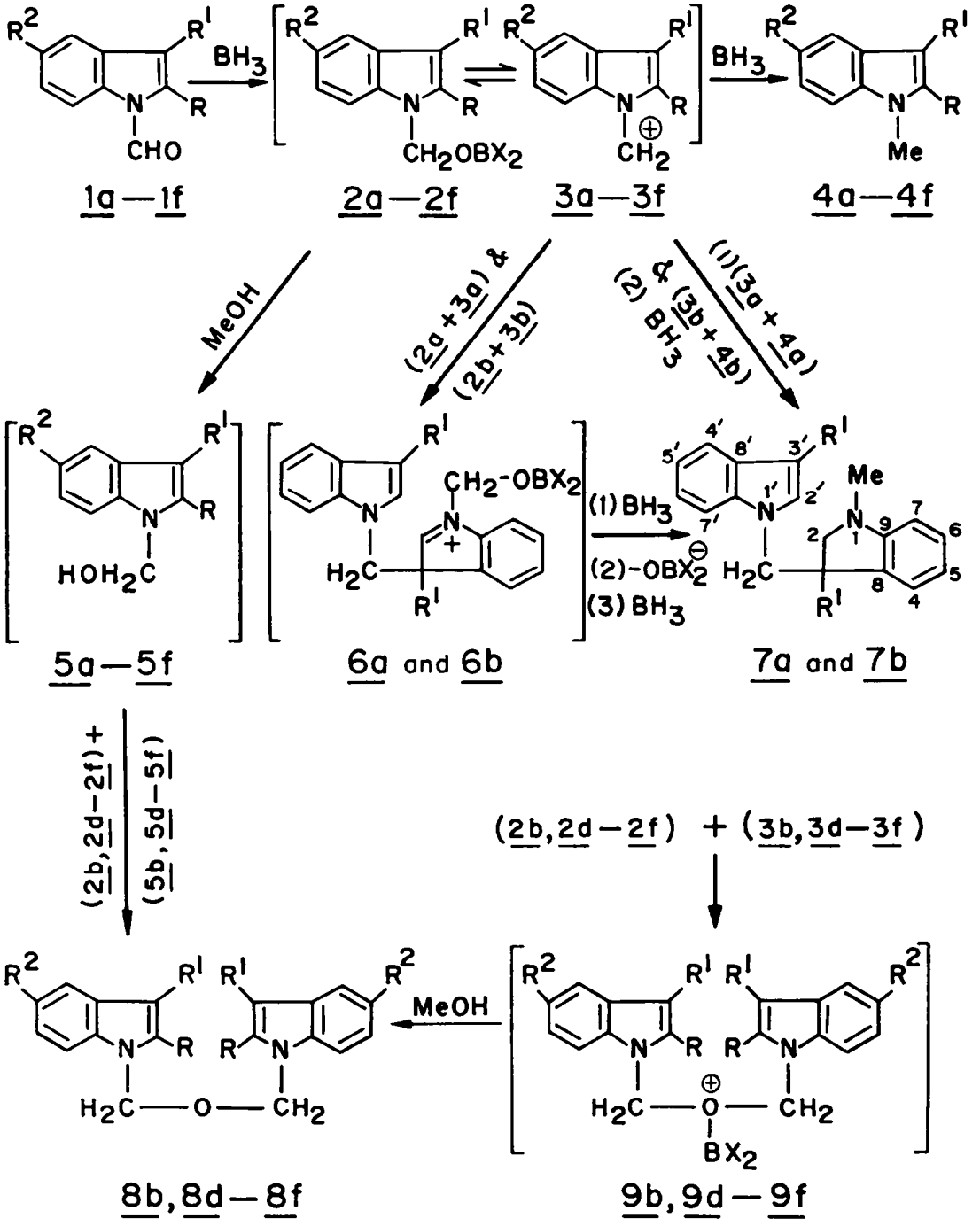
SCHEME I - Mechanisms of Borane / THF Reduction of Indole-1-carboxaldehydes (1)



a, R = R² = H, R¹ = Et
b, R = R² = H, R¹ = Ph
c, R = Ph, R¹ = Me, R² = H
d, R = Ph, R¹ = Et, R² = H
e, R = R¹ = Ph, R² = H
f, R = R¹ = Ph, R² = Me
g, R = R² = H, R¹ = Me
h, R = R¹ = Me, R² = H

X = H or indole unit

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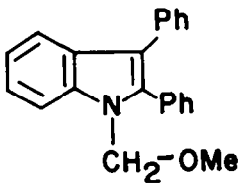

10

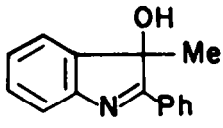

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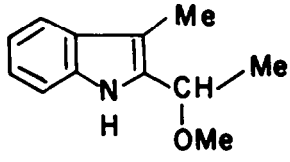
Table 1: Products obtained in the Borane/THF Reduction of Indole-1-carboxaldehydes (1a - 1f)

Starting material	Products	Yield (%)
1a	4a	42
	7a	43
1b	4b	55
	7b	6
	8b	3
1c	4c	72
	11	8
1d	4d	91
	8d	4
1e	4e	70
	8e	6
	10	4
1f	4f	57
	8f	1



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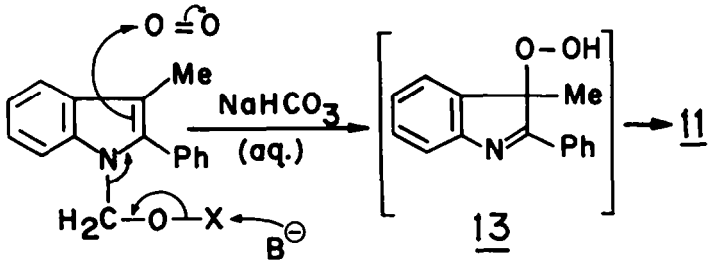

2c, X = BH_2

5c, X = H

SCHEME II

It may be noticed that ether formation took place when 1 had a phenyl group at position 2 or 3 or both (e.g. 1b, 1d - 1f) except 1c (vide infra), but no ether was formed when 1 had only an alkyl group at position 3 (e.g. 1a and 1g[10]) or at positions 2 and 3 (e.g. 1h[10]).

The mechanism of origin of 4 and 7 is similar to that reported earliar[10], but that of 7 may also involve electrophilic substitution of 2 by 3 (Scheme I). A number of mechanisms can be conceived for the formation of 8, such as, nucleophilic attack on 2 by 5 (presumably formed during MeOH treatment), nucleophilic attack by 2 on 3, catalytic effect of BH_3 or BF_3[a]. The observation that ether formation was apparently dependent on the nature of the substituents (vide

[a]Diborane generated externally from $LiAlH_4$ or $NaBH_4$ and $BF_3.OEt_2$ is contaminated with traces of BF_3 which can change the course of a reaction by its catalytic effect[13]. As both borane/THF and BF_3 are known to cleave ethers[14], the possibility of their catalytic effect on the formation of 8 is probably remote.

supra) may provide some support to the first possibility. A methyl substituent at position 2 or 3 or both increases electron density on the nitrogen atom and enhances the rate of solvolysis of 2 to 3. When MeOH was added, very little or none of 2 was possibly left behind to give 5 to form 8. On the other hand, a phenyl substituent at position 2 or 3 cannot increase electron density on the nitrogen atom as effectively as a methyl group, it rather reduces it;[15] and renders solvolysis of 2 less favourable and much slower. When MeOH was added, some of 2 was possibly still left behind to generate 5 and lead to 8.

Although pyridine/borane in CF_3COOH was reported to reduce aldehydes to symmetric ethers, and to unsymmetric ethers with the combination of alcohols,[16] so far as we are aware, there is no record in the literature on the formation of any symmetric ether in the borane/THF reduction of an oxygen function in the absence of an added acid. It may be mentioned here that we obtained earlier the unsymmetric ether (12) from a related reaction,[17] and 10 probably arose as a result of competitive nucleophilic attack by MeOH on 2e or 3e. The involvement of added alcohols in the formation of unsymmetric ethers[16,17] tends to support our proposed mechanism for the origin of 8.

11 probably originated via 2c or 5c under the influence of base by hydrolytic cleavage and autoxidation,[18] since in this particular case, the crude product was treated with aqueous $NaHCO_3$ (Scheme II)[b]. Moreover, as borane/THF is capable of reducing imines to amines,[10,17,20] it must have arisen after the quenching of the former with MeOH[c].

Another point of interest is the fact that although borane/THF reduction of indole derivatives have been reported to yield indolines,[12a,g] we failed to detect any such indolines in our present work or in our earlier studies on indole-4-,[1,22] indole-3-,[17,23] indole-2-[17] and indole-1-carbonyl derivatives.[10]

Finally, the formation of 7 provides unambiguous support to Jackson's theory of electrophilic substitution in 3-substituted indoles.[12a] His more recent findings[18,24] and those of others[25] also support his theory.

The indole-1-carboxaldehydes (1c - 1f) bearing a phenyl group at position 2 did not form the corresponding indolylmethyl indolines probably because of steric hindrance.[27]

The mass spectral fragmentation pattern of 7 is similar to those reported earlier.[10]

EXPERIMENTAL

Melting points are uncorrected. ^1H NMR spectra were recorded on a Nicolet NT 200 (200 MHz) or Varian CFT-20 (80 MHz) spectrometer. ^{13}C NMR spectra were obtained on the latter instrument and are reported in parts per million from Me_4Si. All NMR spectra were recorded in $CDCl_3$, UV spectra in EtOH and IR spectra in KBr disc, unless otherwise mentioned. ^{13}C Assignments which have been made on the basis of correlation with the spectra of other indoles[28] are supported by the observation of C-H coupling but only the completely proton-decoupled spectra are reported. Electron impact mass spectra (EI) were run at 70 eV on a Finnigan 4000 or AEI MS-30 mass spectrometer and chemical ionization mass spectra (CI) on a Finnigan 4000 machine, and peak positions (m/e) are followed by relative abundances in parentheses. Light petrol indicates the fraction b.p.60-80°. Diglyme, tetrahydrofuran (THF) and $BF_3.OEt_2$ were purified[29] just before use. Microanalyses were performed by the staff of the Department.

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[b] Conversion of an indoline-3-hydroperoxide to the corresponding indoline-3-ol was reported to take place in aqueous solution or to be catalyzed by silica gel.[19] The possibility of catalysis by silica gel in our case cannot be ruled out.

[c] Reduction of 11 with both $NaBH_4$ and $LiAlH_4$[21] and the isolation of an indolenine hydroperoxide from a $LiAlH_4$ reduction[2] are also recorded in the literature.

DIBORANE AS A REDUCING AGENT - VI

General Procedure for the Reduction of the Indole-1-carboxaldehydes (1a - 1f) with Borane/THF. The indole-1-carboxaldehydes (1a - 1f)[d] (6 mmole) were reduced with borane/THF (30 mmole) following our earlier procedure[10]. The crude product obtained after removal of MeOH was dissolved in $CHCl_3$ (100 ml), washed with water (3x10ml), dried (Na_2SO_4) and evaporated to dryness under reduced pressure. In case of 1c, the $CHCl_3$ solution of the crude product was washed successively with aqueous $NaHCO_3$ (5%) and H_2O. The residue of the $CHCl_3$ solution was chromatographed on a silica gel column. The remaining part of the procedure is described separately for each compound mentioning the eluting solvents listed below :

3-Ethyl-1-methylindole (4a) : Light petrol; colourless viscous liquid (lit.[30] b.p. 74-76°/0.35 mmHg); λ max (log ϵ) : 223 nm (4.50), 289 (3.79); ^{1}H NMR δ : 6.70 (1H, s, 2-H), 6.9 - 7.3 (4H, m, 4, 5, 6, 7-H), 2.70 (2H, q, J = 7Hz, 3-CH_2), 1.35 (3H, t, J = 7Hz, 3-CH_2-CH_3), 3.58 (3H, s, N-CH_3); picrate, m.p.98-99° (lit.[30] m.p.97-98°).

3-Ethyl-1-methyl-3-(3'-ethylindolyl-1'-methyl)indoline (7a) : Light petrol + AcOEt (49:1); colourless viscous liquid; ν max (neat): 3040, 1600, 1475, 1270, 750 cm^{-1}; ^{1}H NMR δ : 7.42 - 7.54 (1H, m, 4'-H), 7.0 - 7.2 (4H, m, 5',6',7', 7-H), 6.5-6.72 (3H, m, 4,5,6-H), 6.39 (1H, s, 2'-H), 4.08 (2H, s, N-CH_2), 3.17 (1H, d, J_{AB} = 9.2 Hz, 2-H_A), 2.94 (1H, d, J_{AB} = 9.2 Hz, 2-H_B), 2.65 (3H, s, N-CH_3), 2.65 (2H, q, J = 7.45 Hz, 3'-CH_2), 1.76 (2H, q, J = 7.1 Hz, 3-CH_2), 1.20 (3H, t, J = 7.45 Hz, 3'-CH_2-CH_3), 0.79 (3H, t, J = 7.1 Hz, 3-CH_2-CH_3); ^{13}C NMR ppm : 35.47 (N-CH_3), 52.14 (C-2), 50.52 (C-3), 18.08 (3-CH_2), 8.92 (3-CH_2-CH_3), 123.51 (C-4), 117.5 (C-5), 128.1 (C-6), 107.21 (C-7), 132.6 (C-8), 152.81 (C-9), 62.67 (N-CH_2), 125.71 (C-2'), 117.03 (C-3'), 118.28 (C-4'), 121.17 (C-5'), 118.59 (C-6'), 109.42 (C-7'), 127.28 (C-8'), 137.92 (C-9'), 27.07 (3'-CH_2), 14.47 (3'-CH_2-CH_3); EI m/e : 318 (M^+, 13.9), 160 (100), 159 (37.15), 158 (8.33), 145 (8.33), 144 (37.5), 132 (11.11), 131 (11.8), 130 (12.15).

1-Methyl-3-phenylindole (4b) : Light petrol + benzene (9:1); colourless viscous liquid (lit.[31] m.p.62-63°); 1,3,5-trinitrobenzene charge transfer complex (from cyclohexane), dark red needles, m.p.95-97°; ^{1}H NMR δ : 9.19 (3H, s, protons of 1,3,5-trinitrobenzene), 7.61 - 7.85 (1H, m, 4-H), 7.03 - 7.59 (9H, m, Ar-H), 3.75 (3H, s, N-CH_3).

1-Methyl-3-phenyl-3-(3'-phenylindolyl-1'-methyl)indoline (7b) : Light petrol + benzene (1:1); white solid, resolved by fractional crystallization from a mixture of light petrol and benzene (9:1) into 7b and 8b. 7b : white needles, m.p.149°; λ max (log ϵ) : 236 nm (4.38), 262 (4.26), 283 (4.18); ν max : 3000, 1600, 1460, 760 cm^{-1}; ^{1}H NMR δ : 7.84 - 7.88 (1H, m, 4'-H), 7.03 - 7.63 (15H, m, Ar-H), 6.55 - 6.74 (3H, m, 4,5,6-H), 4.70 (2H, s, N-CH_2), 3.53 (2H, s, 2-H), 2.73 (3H, s, N-CH_3); EI m/e : 414 (M^+, 2.01), 209 (16.42), 208 (100), 207 (37.33), 206 (9.08), 193 (20.22), 178 (1.78); CI m/e : 415 (100, MH^+), 208 (84.77), 207 (16.65). (Found : C, 86.90; H, 6.32; N, 6.76. $C_{30}H_{26}N_2$ requires : C, 86.81; H, 6.12; N, 6.58%).

The Symmetric Ether (8b) : colourless needles, m.p.163°; λ max (log ϵ): 235 nm (4.43), 267 (4.33), 293 (4.16); ν max : 1600, 1463, 1447, 1350, 1200, 1045, 900, 730, 690 cm^{-1}; ^{1}H NMR δ : 7.94 - 7.98 (2H, dd, J = 9 and 1.9 Hz, 4-H), 7.63 - 7.67 (2H, dd, J = 9 and 1.9 Hz, 7-H), 7.42 - 7.52 (4H, m, 5, 6-H), 7.27 - 7.35 (10H, m, Ar-H), 7.24 (2H, s, 2-H), 5.49 (4H, s, N-CH_2O); EI m/e : 428 (M^+, 2.07), 224 (3.02), 223 (27.33), 207 (16.19), 206 (100), 193 (57.78), 192 (11.56), 178 (4.87), 165 (23.20); CI m/e : 429 (MH^+, 26.50), 399 (20.25), 224 (31.48), 208 (13.18), 206 (100).

1,3-Dimethyl-2-phenylindole (4c) : Light petrol + benzene (4:1); white needles, m.p.69° (lit.[32] m.p.69°); ^{1}H NMR δ : 7.10-7.71 (9H, m, Ar-H), 3.58 (3H, s, N-CH_3), 2.27 (3H, s, 3-CH_3).

3-Hydroxy-3-methyl-2-phenyl-3H-indole (11) : Benzene; white needles, m.p.147° (lit.[33a,b] m.p.145°); ^{1}H NMR[33b,c] δ: 8.10 (2H, dd, J = 9 and 2 Hz, 2', 6'-H), 7.2-7.4 (7H, m, Ar-H), 1.48 (3H, s, 3-CH_3), 3.63 (1H, s, 3-OH); EI m/e : 223 (M^+, 100), 222 (43.9), 209 (22.21), 208 (94.57), 146 (45.61), 105 (98.54), 104 (29.35). (Found : C, 81.01; H, 5.84; N, 6.00. $C_{15}H_{13}NO$ requires : C, 80.69; H, 5.87; N, 6.28%).

3-Ethyl-1-methyl-2-phenylindole (4d) : Light petrol; colourless oil; ^{13}C NMR ppm: 30.56 (NCH_3), 137.16 (C-2), 115.24 (C-3), 118.92 (C-4), 121.48 (C-5), 118.92 (C-6), 109.2 (C-7), 127.39 (C-8), 137.16 (C-9), 132.18 (C-1'), 128.17 (C-2' and C-6'), 130.44 (C-3' and C-5'), 127.72 (C-4'), 17.79 (3-CH_2), 15.88 (3-CH_2-CH_3); 1,3,5-trinitrobenzene charge transfer complex, dark red needles (from MeOH), m.p.81-82°; ^{1}H NMR δ : 9.25 (3H, s, protons of 1,3,5-trinitrobenzene), 7.08-7.57 (9H, m, Ar-H), 3.55 (3H, s, N-CH_3), 2.69 (2H, q, J = 7.4 Hz, 3-CH_2), 1.20 (3H, t, J = 7.4 Hz, 3-CH_2-CH_3).

[d] Prepared by the procedure described in ref.27b.

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The Symmetric Ether (8d) : Light petrol and benzene (7:3); white needles (from light petrol), m.p.160°; λmax (log ε) : 238 nm (4.55), 294 (4.42); ν max : 2960, 1600, 1465, 1360, 1120, 1020, 1010, 745 cm^{-1}; ^1H NMR δ : 7.60-7.65 (2H, m, 4-H), 7.14-7.38 (16H, m, Ar-H), 5.23 (4H, s, N-CH_2-O), 2.69 (4H, q, J = 7.5 Hz, 3-CH_2), 1.19 (6H, t, J = 7.5 Hz, 3-CH_2-CH_3); EI m/e : 484 (M^+, 2.54), 251 (0.38), 235 (21.55), 234 (100), 221 (0.59), 219 (3.27), 218 (13.56), 217 (5.17), 206 (11.79), 205 (21.94), 204 (13.77).

1-Methyl-2,3-diphenylindole (4e) : Light petrol ; colourless hairy needles, m.p.138° (lit.[34] m.p.137-138°); ^1H NMR δ : 7.69-7.82 (1H, m, 4-H), 7.19-7.31 (13H, m, Ar-H), 3.65 (3H, s, N-CH_3).

The Symmetric Ether (8e) : Light petrol + benzene (6:1); white solid, resolved by fractional crystallization from EtOH into 8e and 10. 8e : silky white needles, m.p.153-154°; λmax (log ε): 239 nm (4.66), 297 (4.44); ν max : 1600, 1460, 1330, 1230, 1145, 1030, 760, 690 cm^{-1}; ^1H NMR δ : 7.7-7.85 (2H, m, 4-H), 7.1-7.5 (26H, m, Ar-H), 5.34 (4H, s, N-CH_2-O); ^{13}C NMR ppm : 71.48 (N-CH_2-O), 120.07 (C-4), 123.17 (C-5), 121.42 (C-6), 110.12 (C-7), 128.31 (C-2', C-5' and C-4"), 130.14 (C-3' and C-5'), 128.12 (C-4'), 128.49 (C-2" and C-6"), 131.36 (C-3" and C-5")[e]; EI m/e : 580 (M^+, 1.49), 299 (1.76), 283 (24.87), 282 (100), 281 (7.28), 280 (11.77), 269 (13.85), 267 (11.47), 254 (4.75). (Found : C, 86.58; H, 5.39; N, 4.65. $C_{42}H_{32}N_2O$ requires: C, 86.87; H, 5.55; N, 4.82%).

The Unsymmetric Methyl Ether (10) : white needles, m.p.121°; λmax (log ε) : 237 nm (4.51), 293 (3.66); ν max : 1600, 1450, 1230, 1120, 1075, 790, 690 cm^{-1}; ^1H NMR δ : 7.77 (1H, d, J = 7.8 Hz, 4-H), 7.57 (1H, d, J = 7.8 Hz, 7-H), 7.17 - 7.37 (12H, m, Ar-H), 5.38 (2H, N-CH_2-O), 3.25 (3H, s, O-CH_3); EI m/e : 313 (M^+, 100), 283 (16.48), 282 (46.63), 281 (3.43), 280 (5.93), 269 (M-ethylene oxide, 21.54), 268 (14.4), 267 (28.04), 254 (1.48). (Found : C, 84.00; H, 5.98; N, 4.45. $C_{22}H_{19}NO$ requires : C, 84.31; H, 6.11; N, 4.47%).

1,5-Dimethyl-2,3-diphenylindole (4f) : Light petrol + benzene (9:1); colourless flakes (from light petrol + benzene), m.p.127-128°; λmax (log ε): 235 nm (4.26), 305 (3.98); ν max : 1600, 1500, 1480, 1370, 720, 695 cm^{-1}; ^1H NMR δ : 6.98-7.49 (13H, m, Ar-H), 3.54 (3H, s, N-CH_3), 2.38 (3H, s, 5-CH_3). (Found : N, 4.63. $C_{22}H_{19}N$ requires; N, 4.71%).

The Symmetric Ether (8f) : Light petrol + benzene (1:1); silky white needles [from petroleum ether (b.p.100-120°)], m.p.181-182°; λmax (log ε): 237 nm (4.65), 301 (4.45); ν max : 3020, 1600, 1465, 1100, 1030, 790, 700 cm^{-1}; ^1H NMR δ : 7.00-7.51 (26H, m, Ar-H), 5.35 (4H, s, N-CH_2-O), 2.46 (6H, s, CH_3); EI m/e : 608 (M^+, 1.05), 313 (68.75), 297 (100), 296 (56.75), 295 (11.21), 294 (18.05), 284 (80.00), 283 (68.00), 282 (25.00), 281 (15.00), 268 (3.15).

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