2*H*-Benzimidazoles (Isobenzimidazoles). Part 3.[1] Thermal Isomerisation of Substituted 2*H*-Benzimidazoles to 1*H*-Benzimidazoles

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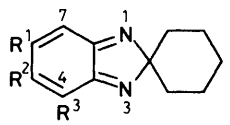
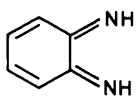
2*H*-Benzimidazole-2-spirocyclohexanes (**1**) when heated undergo a 1,5-sigmatropic rearrangement to 2,3-disubstituted 1*H*-benzimidazoles. A decided effect on the direction of this isomerisation was observed with substituents in the homodiene ring.

We have shown[2] that the readily prepared and stable 2*H*-benzimidazole-2-spirocyclohexane (**1**; $R^1 = R^2 = R^3 = H$) is equivalent in its synthetic potential to an *o*-benzoquinone di-imine (**2**) which has so far eluded[3] all attempts to isolate it as a pure sample. Thus, 2*H*-benzimidazole reacts readily with various nucleophiles (R_2NH, RSH) to give the corresponding 5-mono (**1**; $R^2 = R_2N$, RS, $R^1 = R^3 = H$) or 5,6-disubstituted products (**1**; *e.g.* $R^1 = R^2 = R_2N$, RS, $R^3 = H$) by a 1,4-Michael addition followed by oxidation.[2] This substitution pattern[3b] is predictable on the basis of HMO calculations for *o*-benzoquinone di-imine which is isoelectronic with our system. Alternatively, 4-substitution [*cf.* (**1**)] by a 1,6-Michael addition to a 2*H*-benzimidazole occurs with an electron-withdrawing 5-substituent [*e.g.* (**1**; $R^2 = SO_2R$, NO_2, CF_3)] leading to a 4,5-disubstituted product. Reductive ring opening of (**1**)[a] yields the corresponding *o*-phenylenediamines (**3**) which can be converted



(**1**)



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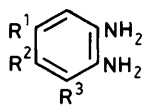
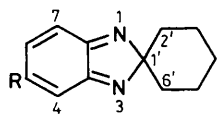


(**3**)

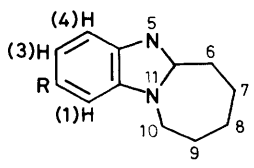
into a wide range of heterocycles[1,2] often with unusual substituents.

We have already reported[4] the thermal 1,5-sigmatropic isomerisation of the parent 2*H*-benzimidazole (**4**; R = H) to the stable tricyclic 1*H*-benzimidazole [1*H*-hexahydroazepino[1,2-*a*]benzimidazole (**5**; R = H)]. This isomerisation of a non-aromatic to a heteroaromatic system appeared to offer a simpler route to 1,2-bridged benzimidazoles than their conventional



(**4**)

heat



(**5**)

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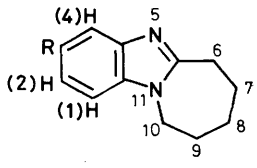
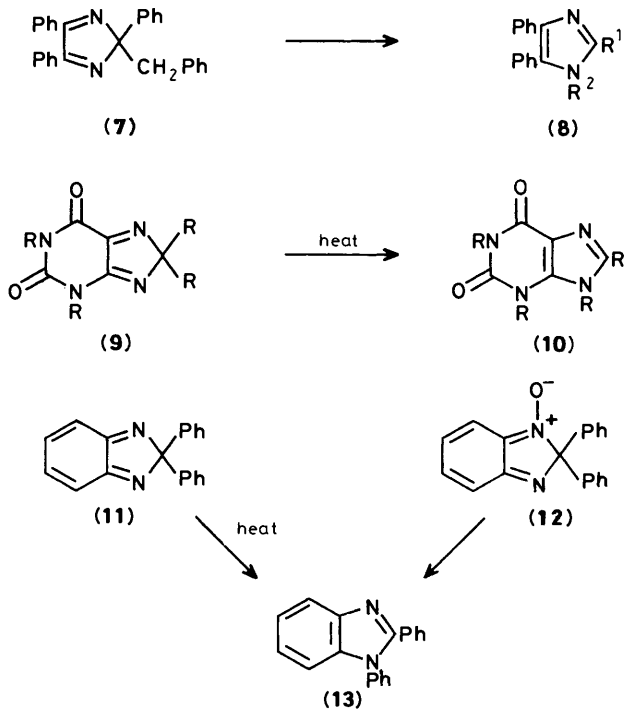


(**6**)

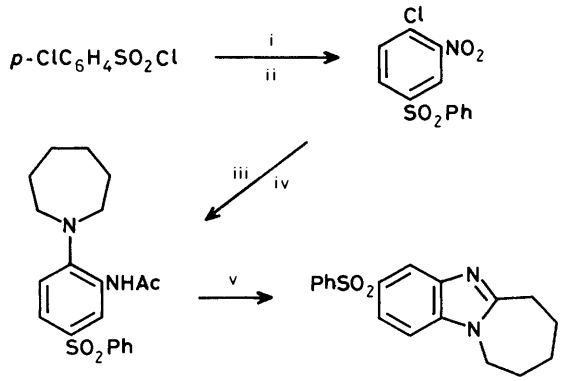


preparation.[5] Analogous rearrangements have been observed in 2*H*-imidazoles[6] to give the corresponding imidazoles [(**7**)→(**8**); R^1 = Ph, $R^2 = CH_2Ph$ or $R^1 = CH_2Ph$, R^2 = Ph] and in xanthines[7] [(**9**)→(**10**)] yielding 7,8-disubstituted derivatives. Similarly we found that, on melting 2,2-diphenyl-2*H*-benzimidazole (**11**), it rearranges quantitatively into 1,2-diphenylbenzimidazole (**13**). A previous observation[8] that benzofuroxan, when heated with diphenyldiazomethane ($Ph_2 > CN_2$), also yields the benzimidazole (**13**) is explicable by virtue of the intermediate formation of the *N*-oxide [(**12**)→(**13**)].

We have now studied intramolecular transpositions of various spiro-2*H*-benzimidazoles with substituents in the homodiene or in the cyclohexyl ring to give 1,2-disubstituted benzimidazoles by migration of the 2′(6′)-spiromethylene group from carbon to nitrogen [*cf.* (**4**)].

Rearrangements of 2H-*Benzimidazoles Substituted in the Homodiene Ring.*—The 5-nitro derivative (**4**; R = NO_2) rearranged when heated in *o*-dichlorobenzene to give an inseparable mixture (85%) of the isomeric nitrobenzimidazoles (**5**) and (**6**; R = NO_2) since either of the spiromethylene groups is free to migrate [*cf.* (**4**); 2′ or 6′]. The isomeric ratio of (**5**):(**6**) (63:37) was estimated on the reasonable assumption that the low field signal at δ 8.6 is due to 4-H in the isomer (**6**). The 5-

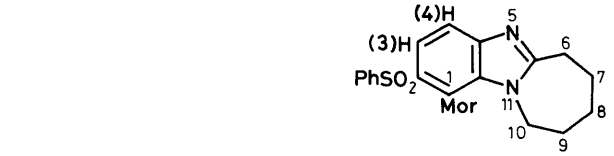
phenylsulphonyl derivative (**4**; R = SO_2Ph) gave under similar conditions an isomeric mixture (**5**) and (**6**; R = SO_2Ph) which was separable by fractional crystallisation. On assigning the low field signal at δ 8.3 (1 H, d, J = 2 Hz, 4-H) to the isomer corresponding to (**6**; R = SO_2Ph) we estimated the ratio of the benzimidazoles (**5**) and (**6**) as 65:35. This was in reasonable agreement with a ratio of 70:30 obtained by h.p.l.c. separation of the isomers. The structure of one of the isomers (**6**; R = SO_2Ph) was confirmed by an unambiguous synthesis as outlined in the Scheme. The oxidative ring-closure[5] with HCO_2H–



Scheme. *Reagents:* i, HNO_3–H_2SO_4; ii, C_6H_6–$AlCl_3$; iii, $C_6H_{13}N$–EtOH; iv, Pd–H_2–Ac_2O; v, H_2O_2–HCO_2H

H_2O_2 in the final step occurred in high yield and the product proved to be identical with the minor isomer (**6**). It also supported our general low-field assignment for 4-H in analogous structures. The sulphones (**4**; R = p-$MeC_6H_4SO_2$ and $MeSO_2$) also rearranged in high yields (88 and 95%, respectively) giving isomeric mixtures (**5**) and (**6**) in the ratios 65:35 and 71:29, respectively. The proportions were again estimated on the basis of the peak area of the low-field 4-H-signal in the isomer (**6**) as described above.

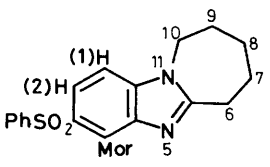
We also studied the rearrangement of some disubstituted derivatives. Thus 4-morpholino-5-phenylsulphonyl-2*H*-benzimidazole (**14**) rearranged quantitatively in hot dichlorobenzene to give a mixture of the expected isomers (**15**) and (**16**). Chromatographic separation furnished two white compounds of the same molecular ion m/z 411 $(M)^+$ and different m.p.s in the ratio 72:28. Their ^{1}H n.m.r. spectra showed certain broad



(**14**)

Mor = Morpholino

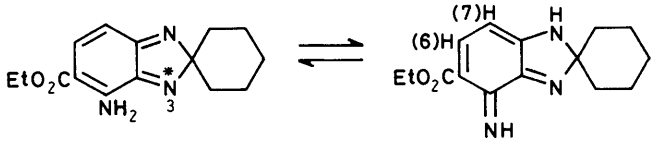
(**15**)



(**16**)

similarities to the previous isomers (**5**) and (**6**) which helped to assign the structures. For instance, in both pairs the predominant isomer had the lower m.p. and its aromatic protons (^{1}H n.m.r.) were closer together in the aromatic region than those of its isomeric partner: 3-H at δ 8.0 showed as a doublet (J 9 Hz) and the 4-H signal was overlapping with that for the $PhSO_2$ protons (δ 8.0—7.75) in the major constituent. The minor isomer had, by contrast, a more expanded aromatic region namely doublets for the 2-H and 1-H protons at δ 8.15 and 7.25 (J = 9 Hz). On this basis the structural assignment for the major and the minor product as (**15**) and (**16**) respectively appears feasible by analogy.

Another disubstituted example was 4-amino-5-ethoxycarbonyl-2*H*-benzimidazole (**17**) obtained from the 5-ethoxycarbonyl derivative (**4**; R = CO_2Et) with ethanolic ammonia as a dark red solid which suggested tautomeric participation (**17**)⇌(**18**). This was confirmed by two replaceable signals (D_2O) in the ^{1}H n.m.r. at δ 8.1 (=NH) and 6.3 (–NH). The 2*H*-benzimidazole (**17**) when heated in *o*-dichlorobenzene gave by chromatography (SiO_2; light petroleum–ethyl acetate) two isomeric products structurally indicative of a sigmatropic



(**17**) (**18**)

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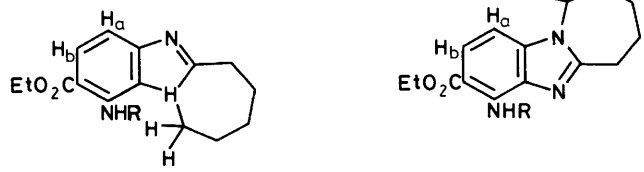
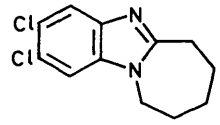


(**19**) (**20**)

conversion. Assignment became possible when each isomer was converted into its formyl derivative (**19**) and (**20**) (R = CHO). The isomer in which the ring protons H_a and H_b appeared as two close doublets (δ 7.5 and 7.85), since they are both under the influence of electron-attracting groups (CO_2Et, –N=), was recognised as the 6,7-disubstituted benzimidazole (**19**). By contrast, the compound in which H_a and H_b are well separated doublets (δ 6.9 and 7.9 respectively), since they are adjacent to groups of differing electronic tendency (**20**; >N– and CO_2Et), can reasonably be regarded as the 4,5-disubstituted derivative (**20**; R = CHO). The coupling of the protons in NH and CHO of the isomers (**19**) and (**20**) (R = CHO) is noteworthy. In compound (**20**; R = CHO) the NH and CHO protons each appear as a doublet at δ 11.0 and 10.45, respectively (J 9 Hz), with expected behaviour on deuteriation. In the isomer (**19**; R = CHO), however, the NH and CHO signals are both broad singlets at δ 9.85 and 8.5 respectively. The coupling here is indistinct possibly because of steric crowding of the formamido group [*cf.* (**19**; R = CHO)]. The dominant isomer (74%) is the 6,7-disubstituted benzimidazole (**19**), *i.e.* migration of the spiromethylene is favoured towards the ring nitrogen N-3 as in the previous cases [*cf.* (**14**)→(**15**); (**4**; R = NO_2, SO_2Ph)→(**5**)].

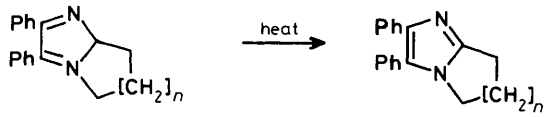
The 5,6-dichloro derivative (**1**; $R^1 = R^2 = Cl$, $R^3 = H$) rearranged smoothly to the expected benzimidazole (**21**).



(**21**)

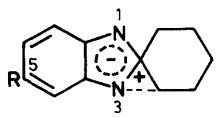
The 5-phenoxy-2*H*-benzimidazole[2] (**4**; R = PhO) bearing an electron-releasing substituent rearranged when heated to 170 °C (m.p. 163 °C) for 30 min. Work-up gave a mixture of isomers (**5**) and (**6**; R = PhO). We assigned, by analogy with previous observations (*cf.* above), the lowest chemical shift in the ^1H n.m.r. spectrum to 4-H in isomer (**5**; R = PhO) at δ ($CDCl_3$) 7.65 (d, $J_{3,4}$ 9 Hz). On this basis the isomeric ratio of (**5**):(**6**; R = PhO) was assessed as 40:60. The predominance of isomer (**6**) is as expected in contrast with rearrangements in which electron-withdrawing substituents (NO_2, SO_2Ph) are present in position 3 of the cyclohexadiene ring (see above).

We believe that the thermal rearrangement of the spiro-2*H*-benzimidazoles [*e.g.* (**4**)→(**5**) + (**6**)] which is little influenced by solvents (dichlorobenzene, light petroleum, DMSO) or in the melt is a concerted intramolecular process. The reaction as mentioned, is closely analogous to the sigmatropic changes observed in various 2*H*-imidazoles [*e.g.* (**11**)→(**13**); (**22**)→(**23**)]



(**22**) (**23**)

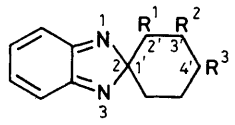
for which a concerted mechanism was confirmed.[6b] It is likely that the 2*H*-benzimidazole rearrangement involves a charged intermediate of the type (**24**) which would be stabilised by electron-withdrawing groups in position 5 (**24**; R = NO_2, SO_2Ph). This would account for the observed bias in the migration of the cyclohexyl methylene (CH_2) towards N-3. The converse would be expected for the electron-releasing phenoxy group [(**24**; R = PhO); *cf.* Table] which is indeed the case. An



(**24**)

analogous type of transition state was postulated for the 1,5-shift in 2*H*-imidazoles[6c] where the electronic nature of the substituents also influenced the rearrangement.

Rearrangements of 2H-*Benzimidazoles with Substituents in the Cyclohexyl Ring.*—When the 2′-methylcyclohexyl derivative (**25**; $R^1 = Me$, $R^2 = R^3 = H$) was refluxed in light petroleum (b.p. 100—120 °C) only one product could be isolated (40%). Since its methine multiplet at δ 4.80 (H_a) appears at a lower field than its lowest methylene multiplet due to CH_{2b} (δ 3.18) we assign the benzimidazole structure (**26**) to this compound. Rearrangement of the 3′-methylspiro-2*H*-benzimidazole (**25**; $R^1 = R^3 = H$, $R^2 = Me$) by melting the compound gave an inseparable mixture of isomeric azepinobenzimidazoles (**27**; $R^1 = Me$, $R^2 = R^3 = H$ and $R^1 = R^2 = H$, $R^3 = Me$). Its composition (*ca.* 1:1) was inferred from two overlapping methyl doublets at δ 0.85 (dd) apart from the expected peaks and



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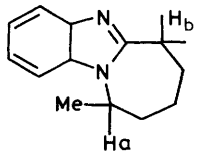

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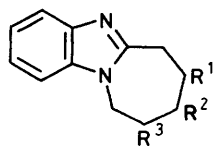


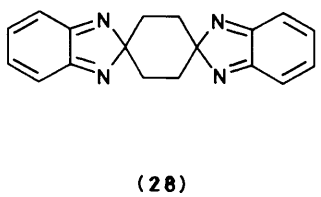
(**27**)

Table. Sigmatropic rearrangement of substituted 2*H*-benzimidazoles into benzimidazoles

2*H*-Benzimidazole-2-spirocyclohexane	Reaction time (h)	Benzimidazoles: Yield (%)	Isomer ratio	M.p. (°C)
5-NO_2(**4**; R = NO_2)	3	70	(**5**):(**6**) = 63:37; R = NO_2	176—180[c]
5-SO_2Ph(**4**; R = SO_2Ph)	3	90	(**5**):(**6**) = 63:37;[a] R = SO_2Ph	(**5**); 185—186
			(**5**):(**6**) = 72:28[b]	(**6**); 200—201
(**14**)	0.5	100	(**15**):(**16**) = 72:28	(**15**); 240—242
				(**16**); 285—287
5-*p*-$MeC_6H_4SO_2$(**4**; R = *p*-$MeC_6H_4SO_2$)	3	88	(**5**):(**6**) = 65:35,[a] R = *p*-$MeC_6H_4SO_2$	176—185[c]
5-$MeSO_2$(**4**; R = $MeSO_2$)	0.5	95	(**5**):(**6**) = 71:29,[a] R = $MeSO_2$	140—155[c]
5,6-Dichloro-(**1**; $R^1 = R^2 = Cl$, $R^3 = H$)	0.5	75	One isomer (**21**)	(**21**); 176—177
2′-Me(**25**; $R^1 = Me$, $R^2 = R^3 = H$)	1	40	One isomer (**26**)	(**26**); 80
3′-Me(**25**; $R^2 = Me$, $R^1 = R^3 = H$)	1	30	*ca.* 1:1[a] (**27**; $R^1 = Me$, $R^2 = R^3 = H$ and $R^1 = R^2 = H$, $R^3 = Me$)	160—170[c]
4′-Me(**25**; $R^3 = Me$, $R^1 = R^2 = H$)	1	30	One isomer (**27**; $R^2 = Me$, $R^1 = R^3 = H$)	(**27**); 210
(**28**)	1	5	One isomer (**29**)	(**29**); 225
(**31**)	0.5	98	One isomer (**32**)	(**32**); 186
5-PhO(**4**; R = PhO)	0.5	22.5	(**5**):(**6**) = 40:60 (R = PhO)	110—120[c]

[a] Based on ^1H n.m.r. analysis of the mixture. [b] Based on h.p.l.c. separation. [c] M.p. of isomeric mixture.

elemental analysis. The 4′-methyl isomer (**25**; $R^1 = R^2 = H$, $R^3 = Me$) rearranged in refluxing *o*-dichlorobenzene to give, as expected, only one product, namely the azepinobenzimidazole (**27**; $R^1 = R^3 = H$, $R^2 = Me$) in 30% yield. In the same solvent the bis-2*H*-benzimidazole (**28**) gave mainly tar and only a small quantity of a benzimidazole (5%) to which we ascribe the angular diazocine structure (**29**) because of two methylene triplets at δ 4.06 and 3.08 ($4H_a$ and $4H_b$, *J* 7 Hz, respectively) apart from the required aromatic protons in the ^1H n.m.r. at δ 7.40 (8 H, m). The alternative linear structure would have a different 'methylene spectrum' since it possesses a plane of symmetry (**30**). The most efficient isomerisation occurred when the spiroadamantyl derivative (**31**) was heated to its melting point (170 °C) to give the homoaza-adamantane (**32**) in almost quantitative yield (98%).



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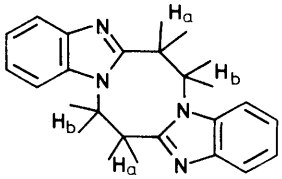

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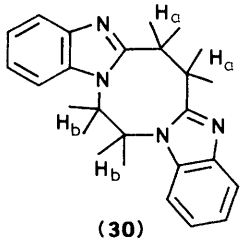

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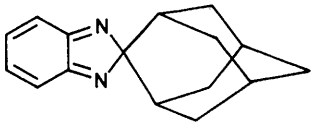

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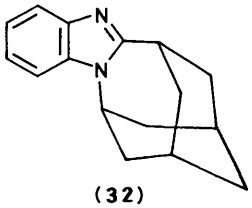

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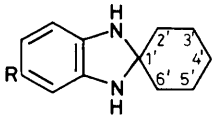

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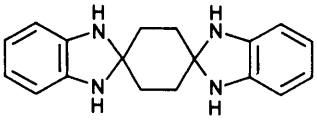

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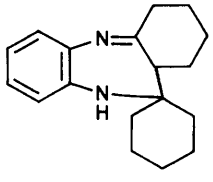

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Experimental

I.r. spectra were recorded for mulls between sodium chloride plates with a Perkin-Elmer 297 or 357 spectrometer, n.m.r. spectra with a Varian EM 360 (60 MHz) or Bruker spectrospin (360 MHz) spectrometer using TMS as internal standard and, unless otherwise stated are at 90 MHz. Microanalyses (C, H, N) were carried out by Butterworth Lab. Ltd. For column chromatography CAMAG basic alumina (pH 9.3—9.7, 100—250 mesh) (Fisons Ltd.) or silica M.F.C. 60—120 mesh (BDH Ltd.) were employed. Light petroleum refers to the fraction b.p. 60—80 °C.

Preparation of 2H-*Benzimidazole*-2-*spirocyclohexanes*.—(*a*) The 5-phenylsulphonyl- (**4**; $R = SO_2Ph$), 4-morpholino-5-phenylsulphonyl- (**14**), 5-*p*-tolylsulphonyl- and 5-methylsulphonyl- (**4**; $R = p\text{-}MeC_6H_4SO_2$ or $MeSO_2$) 2*H*-benzimidazoles have been described.[2]

(*b*) The 5-nitro-2*H*-benzimidazole-2-spirocyclohexane (**4**; $R = NO_2$) was obtained by heating equimolar quantities of 4-nitrophenylenediamine and cyclohexanone in sulpholane for 2 h on a water-bath. The mixture was poured into water and the product filtered off. Recrystallisation from ethanol gave the *nitrodihydrobenzimidazole*-2-*spirocyclohexane* (**33**; $R = NO_2$), m.p. 164 °C (75%) (Found: C, 61.8; H, 6.45; N, 17.8. $C_{12}H_{15}N_3O_2$ requires: C, 61.8; H, 6.5; N, 18.0%); $\nu_{max.}$ 3 380 and 3 160 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.75 and 6.57 (NH removed with D_2O), 6.92 (d, 4-H), 7.53 (d, 6-H), 6.23 (d, 7-H), and 1.62 (10 H, br). The dihydro compound when stirred in dichloromethane with activated MnO_2 (5 × excess by weight) at room temperature for 1 h gave the 5-*nitro*-2H-*benzimidazole*-2-*spirocyclohexane* by the usual procedure.[2] It had m.p. 100 °C (85%) (Found: C, 61.8; H, 5.7; N, 18.4. $C_{12}H_{13}N_3O_2$ requires C, 62.3; H, 5.7; N, 18.2%).

(*c*) 4-*Amino*-5-*ethoxycarbonyl*-2H-*benzimidazole* (**17**). A mixture of ethyl 3,4-diaminobenzoate[9] (10.0 g) and cyclohexanone (50 ml) in sulpholane (50 ml) was heated for 4 h on a water-bath. Work-up as in (*b*) gave 5-*ethoxycarbonyl*-1,3-*dihydro*-2H-*benzimidazole*-2-*spirocyclohexane* (**33**; $R = CO_2Et$) (75%), m.p. 126 °C (Found: C, 69.1; H, 7.95; N, 10.85. $C_{15}H_{20}N_2O_2$ requires C, 69.2; H, 7.7; N, 10.6%). It was oxidised with MnO_2 (30 g) in dichloromethane [*cf.* (*b*)] at room temperature for 1 h and then filtered. The filtrate was evaporated to give the 5-*ethoxycarbonyl*-2H-*benzimidazole* (**4**; $R = CO_2Et$) (90%), m.p. 66 °C (Found: C, 69.85; H, 7.2; N, 11.0. $C_{15}H_{18}N_2O_2$ requires C, 69.75; H, 7.0; N, 10.85%). The product (10 g) dissolved in ethanol (50 ml) was added to a saturated ethanolic solution of ammonia (25 ml) and the stirred mixture set aside for 6 h at 0—10 °C. MnO_2 (20 g) was then added and stirring continued overnight. The mixture was filtered and the filtrate evaporated to give a crude oil product which was chromatographed on alumina using light petroleum–ethyl acetate (1 : 5) as eluant. The main band gave a bright red solid which was recrystallised from light petroleum to give the 4-*amino*-5-*ethoxycarbonyl*-2H-*benzimidazole* (**17**) (73%), m.p. 100—101 °C, $\nu_{max.}$ 3 460, 3 380, 3 325, and 3 260 (NH_2), and 1 675 cm^{-1} (C=O); δ_H(360 MHz, $CDCl_3$) 8.1 (1 H, exchangeable with D_2O, br s, =NH), 7.55 (1 H, d, *J* 9Hz, 6-H), 6.5 (1 H, d, *J* 9 Hz, 7-H), 6.3 (1 H, exch. in D_2O, br s, NH), 4.3 (2 H, q, *J* 7 Hz, OCH_2CH_3), 1.95 (4 H, d, cyclohexyl), 1.85—1.60 (6 H, br t, cyclohexyl), and 1.4 (3 H, t, *J* 7 Hz, OCH_2CH_3) (Found: C, 65.8; H, 6.9; N, 15.2. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%).

(*d*) *Methyl*-2H-*benzimidazole*-2-*spirocyclohexanes*. Equimolar amounts of *o*-phenylenediamine and the required methylcyclohexanone were heated in sulpholane on a water-bath for 2 h. The mixture was poured into cold water and the product filtered off, washed, dried, and either recrystallised from ethanol or chromatographed over alumina with benzene as eluant. The following methyl-1,3-dihydro-2*H*-benzimidazole-2-spirocyclohexanes (**33**; R = H) were prepared: 2′-*methyl* (45%), m.p. 60 °C (Found: C, 77.1; H, 13.3; N, 8.9); $\nu_{max.}$ 3 410 and 3 350 cm^{-1} (NH); $\delta_H(CDCl_3)$ 3.39 (1 H, D_2O exch., NH), 6.45 (3 H, br s, ArH), 1.39 (9 H, br), and 0.90 (d, CH_3). 3′-*Methyl* (55%), m.p. 72 °C (Found: C, 77.3; H, 14.2; N, 9.2); $\nu_{max.}$ 3 360 and 3 290 cm^{-1} (NH); $\delta_H(CDCl_3)$ 4.00 (1 H, D_2O exch., s, NH), 6.40 (3 H, br s, ArH), 1.5 (9 H, br), and 0.86 (d, CH_3). 4′-*Methyl* (98%), m.p. 108 °C (Found: C, 77.55; H, 13.85; N, 9.4); $\nu_{max.}$ 3 360 and 3 270 cm^{-1} (NH); $\delta_H(CDCl_3)$ 3.60 (1 H, D_2O exch., 5, NH), 6.52 (3 H, br s, ArH), 1.50 (9 H, br), and 0.98 (d, CH_3) ($C_{13}H_{18}N_2$ requires C, 77.2; H, 13.85; N, 9.0%). The above methyl derivatives were stirred with MnO_2 in dichloromethane at room temperature for

15 h to give the oxidation products in *ca.* 90% yield, The following methyl-2*H*-benzimidazole-2-spirocyclohexanes were obtained: *2′-methyl* (**25**; R^1 = Me, R^2 = R^3 = H), m.p. 40 °C; $\nu_{max.}$ 1 530 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 7.10 (4 H, m, ArH), 1.80 (9 H, m), and 0.10 (d, CH_3) (Found: C, 77.7; H, 8.25; N, 14.0). *3′-Methyl* (**25**; R^1 = R^3 = H, R^2 = Me), m.p. 95 °C; $\nu_{max.}$ 1 530 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 7.02 (4 H, m, ArH), 2.00 (9 H, m), and 0.95 (d, CH_3) (Found: C, 77.7; H, 8.4; N, 14.3). *4′-Methyl* (**25**; R^1 = R^2 = H, R^3 = Me), m.p. 74 °C; $\nu_{max.}$ 1 525 cm^{-1}; $\delta_H(CDCl_3)$ 7.08 (4 H, m, ArH), 1.85 (9 H, m), and 1.05 (d, CH_3) (Found: C, 78.0; H, 8.5; N, 14.1. $C_{13}H_{16}N_2$ requires C, 77.9; H, 8.05; N, 14.0%).

(*e*) *Dispiro*(2H-*benzimidazole*-2,1′-*cyclohexane*-4,2″-[2H]-*benzimidazole*). Cyclohexane-1,4-dione and *o*-phenylenediamine (2 equiv.) when heated in ethanol under reflux for 10 h with removal of solvent gave a nearly pure product. This was purified on Al_2O_3 as above to give the tetrahydrodispirobenzimidazole (**34**), m.p. 225 °C (98%); $\nu_{max.}$ 3 350 and 3 270 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.32 (8 H, m, ArH), 5.58 (1 H, D_2O exch., s, NH), and 1.79 (8 H) (Found: C, 73.5; H, 6.6; N, 18.8. $C_{18}H_{20}N_4$ requires C, 74.0; H, 6.9; N, 19.2%). Oxidation (MnO_2 in CH_2Cl_2) gave the *dispiro*-2H-*benzimidazole* (**28**) (95%); m.p. 250 °C (decomp.); $\nu_{max.}$ 1 530 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 7.38 (8 H, m, ArH) and 3.17 (8 H, s) (Found: C, 75.0; H, 6.0; N, 19.2. $C_{18}H_{16}N_4$ requires C, 74.9; H, 5.6; N, 19.4%).

(*f*) 2H-*Benzimidazole*-2-*spiro*-1′-*adamantane* (**31**). This was prepared from equimolar quantities of *o*-phenylenediamine and adamantanone under conditions similar to those described for (*e*). The *dihydro derivative* had m.p. 126 °C (80%); $\nu_{max.}$ 3 400 and 3 275 cm^{-1} $\delta_H(CDCl_3)$ 6.55 (4 H, s, ArH), 4.05 (2 H, D_2O exch., s, NH), 1.82 (14 H, m) (Found: C, 79.6; H, 8.3; N, 11.4. $C_{16}H_{20}N_2$ requires C, 79.8; H, 8.4; N, 11.6%). 2H-*Benzimidazole*-2-*spiro*-1′-*adamantane* (**31**) had m.p. 142 °C (95%); $\nu_{max.}$ 1 525 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 7.10 (4 H, m, ArH), 2.75 (1 H, br s), 2.52 (2 H, br s), 2.00 and 1.82 (9 H, m), and 1.15 (2 H, m) (Found: C, 80.6; H, 7.8; N, 11.6. $C_{16}H_{18}N_2$ requires C, 80.7; H, 7.6; N, 11.8%).

(*g*) 5,6-*Dichloro*-2H-*benzimidazole* (**1**; R^1 = R^2 = Cl, R^3 = H). A solution of 4,5-dichloro-*o*-phenylenediamine (8.9 g), in cyclohexanone (25 ml) was heated on a water-bath for 15 min. The solvent was removed and the oily residue chromatographed on alumina (light petroleum–ethyl acetate). The first band yielded the 7,8-*dichloro*-1H-2,3-*dihydrobenzodiazepine*-2-*spirocyclohexane* (**35**) (0.84 g, 5%), m.p. 142—144 °C (from light petroleum); $\nu_{max.}$ 3 375 and 3 250 (NH) and 1 640 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 7.4 (1 H, s, ArH), 6.8 (s, ArH), 4.0—3.6 (1 H, D_2O exch., br s, NH), 2.7—2.3 (3 H, aliph. H), and 2.1—1.2 (16 H, m, aliph. H) (Found: C, 63.9; H, 6.5; N, 8.3. $C_{18}H_{22}Cl_2N_2$ requires C, 64.1; H, 6.6; N, 8.3%). The second band gave the 5,6-*dichloro*-1,3-*dihydro*-2H-*benzimidazole*-2-*spirocyclohexane* (11.6 g, 90%), m.p. 133—134 °C (from light petroleum); $\nu_{max.}$ 3 350 (NH) and 1 500 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 6.5 (2 H, s, ArH), 3.9 (2 H, br s, D_2O exch., NH), and 1.8—1.2 (10 H, br s, aliph. H) (Found: C, 56.2; H, 5.5; N, 11.9. $C_{12}H_{14}Cl_2N_2$ requires C, 56.05; H, 5.5; N, 10.9%). Oxidation with MnO_2 in dichloromethane at room temperature for 1 h and work-up [*cf.* (*b*)] gave 5,6-*dichloro*-2H-*benzimidazole*-2-*spirocyclohexane* (**1**; R^1 = R^2 = Cl, R^3 = H) (95%), m.p. 121—123 °C (from light petroleum); $\delta_H(CDCl_3)$ 7.5 (2 H, s, ArH) and 2.21—1.5 (10 H, br d, aliph. H) (Found: C, 56.4; H, 4.9; N, 11.1. $C_{12}H_{12}Cl_2N_2$ requires C, 56.5; H, 4.7; N, 11.0%).

Rearrangements of 2H-*Benzimidazoles: General Procedure.*—A solution of the required substituted spiro-2*H*-benzimidazole (10 mmol) in *o*-dichlorobenzene (30 ml) was heated under reflux under nitrogen for 1—3 h. The solvent was removed and the residue chromatographed on alumina. The 3′-methyl-2*H*-benzimidazole and 2*H*-benzimidazole-2-spiro-2′-adamantane were pyrolysed dry on an oil-bath (kept at 170 °C) for 30 min. For yields, m.p.s and isomer ratios see Table.

(*a*) The 5-nitro-2*H*-benzimidazole (**4**; R = NO_2) gave a mixture of two isomers as yellow needles (70%); *m/z* 231; $\nu_{max.}$ 1 620 (C=N) and 1 515 and 1 335 cm^{-1} (NO_2) (Found: C, 62.0; H, 5.5; N, 17.6. $C_{12}H_{13}N_3O_2$ requires C, 62.3; H, 5.7; N, 18.2%).

(*b*) 5-Phenylsulphonyl-2*H*-benzimidazole gave the two isomers by fractional crystallisation of the mixture from ethyl acetate. The *2-phenylsulphone isomer* (**5**; R = SO_2Ph), $\nu_{max.}$ 1 300 and 1 150 cm^{-1} (SO_2); δ_H(90 MHz) 8.0 (3 H, m, ArH), 7.75 (2 H, s, ArH), 7.45 (3 H, m, ArH), 4.2 (2 H, d, aliph. H), 3.1 (2 H, d, aliph. H), and 1.9 (6 H, br s, aliph. H) (Found: C, 66.0; H, 5.6; N, 8.5. $C_{18}H_{18}N_2O_2S$ requires C, 66.2; H, 5.6; N, 8.6%). The *3-phenylsulphone isomer* (**6**; R = SO_2Ph) was obtained with dichloromethane–light petroleum; $\delta_H(CDCl_3)$ 8.3 (d, *J* 2 Hz, H-4) [*cf.* (**6**)], 7.9 (3 H, m, ArH), 7.4 (4 H, m, ArH), 4.15 (2 H, d, aliph.), 3.1 (2 H, d, aliph. H), and 1.85 (6 H, br s, aliph. H). It was unambiguously prepared as follows (*cf.* Scheme). Hexahydroazepine (14 ml, 0.12 mol) was added dropwise with stirring to a solution of 4-chloro-3-nitrophenyl phenyl sulphone (16.0 g, 54 mmol) in ethanol (100 ml) and the mixture was heated under reflux for 0.5 h. Cooling in ice produced a yellow precipitate which was filtered off. 4-*Hexahydroazepin*-1-*yl*-3-*nitrophenyl phenyl sulphone* (17.3 g, 90%) had m.p. 119—120 °C, $\nu_{max.}$ 1 600 (C=C), 1 550 and 1 360 (NO_2) 1 310, and 1 150 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 8.3 (1 H, d, *J* 3 Hz, ArH), 8.0—7.7 (3 H, m, ArH), 7.55 (3 H, dd, *J* 5.2 Hz ArH), 7.1 (1 H, d, *J* 9 Hz ArH), 3.3 (4 H, t, aliph.), and 1.9—1.4 (8 H, br d, aliph.) (Found: C, 59.8; H, 5.7; N, 8.25. $C_{18}H_{20}N_2O_4S$ requires C, 60.0; H, 5.6; N, 7.8). The nitro compound (2.0 g, 5.6 mmol) was hydrogenated in ethanol (150 ml) at atmospheric pressure in the presence of Pd/C. The mixture was filtered and the filtrate evaporated to afford a residue which was recrystallised from petroleum (b.p. 80—100 °C)–ethyl acetate to give 3-*amino*-4-*hexahydroazepin*-1-*ylphenyl phenyl sulphone* (71%, 1.3 g), m.p. 118—191 °C; $\nu_{max.}$ 3 450, 3 350 (NH_2), 1 310, and 1 150 cm^{-1} (SO_2); δ_H(60 MHz, $CDCl_3$) 7.9 (2 H, dd, *J* 8 Hz, ArH), 7.7—7.1 (5 H, m, ArH), 7.0 (1 H, d, *J* 9 Hz, ArH), 4.1 (2 H, br s, D_2O exch.), 3.0 (4 H, br s, aliph. H), and 1.75 (8 H, br s, aliph. H) (Found: C, 65.4; H, 6.9; N, 8.6. $C_{18}H_{22}N_2O_2S$ requires C, 65.4; H, 6.7; N, 8.5%). On reflux in acetic anhydride for 5 min the *acetyl derivative* (54%), m.p. 128—129 °C, was obtained; $\nu_{max.}$ 3 300 (NH), 1 690 (C=O), 1 300, and 1 150 cm^{-1} (SO_2) (Found: C, 64.3; H, 6.7; N, 7.8. $C_{20}H_{24}N_2O_3S$ requires C, 64.5; H, 6.5; N, 7.5%). A solution of the *N*-acetyl derivative (0.5 g, 1.34 mmol) in a mixture of formic acid (3 ml, 98%) and hydrogen peroxide (1.5 ml, 30%) was heated on a steam-bath. When the vigorous reaction had subsided the mixture was kept for 15 min at 100 °C and then cooled and neutralised with ammonium hydroxide solution (*d* 0.88). Extraction with chloroform gave 3-*phenylsulphonyl*-6H-7,8,9,10-*tetrahydroazepino*[1,2-a]*benzimidazole* (**6**; R = SO_2Ph) (0.39 g, 90%), m.p. 199—200 °C (from light petroleum–dichloromethane) identical (i.r., n.m.r, and mixed m.p.) with the above 3-sulphone isomer (Found: C, 66.2; H, 5.6; N, 8.5%).

(*c*) 4-Morpholino-5-phenylsulphonyl-2*H*-benzimidazole rearranged quantitatively to an isomeric mixture which was separated by chromatography on silica with ethyl acetate to give 1-*morpholino*-2-*phenylsulphonyl*-6H-*tetrahydroazepino*[1,2-a]*benzimidazole* (**15**), m.p. 240—242 °C; $\nu_{max.}$ 1 290 and 1 150 cm^{-1} (SO_2); δ_H(90 MHz, $CDCl_3$) 8.0 (1 H, d, *J* 9 Hz, 3-H), 7.75 (3 H, m, ArH), 7.55 (3 H, m, ArH), 4.6 (2 H, d, aliph. H), 3.7—2.7 (10 H, m, aliph. H), and 1.85 (6 H, s, aliph. H) (Found: C, 64.2; H, 6.2; N, 10.3) and 4-*morpholino*-3-*phenylsulphonyl*-6H-*tetrahydroazepino*[1,2-a]*benzimidazole* (**16**), m.p. 285—287 °C (ethyl acetate); $\nu_{max.}$ 1 290 and 1 140 cm^{-1} (SO_2); δ_H(90 MHz, $CDCl_3$) 8.15 (1 H, d, *J* 9 Hz, 2-H), 7.8 (2 H, m, ArH), 7.45 (3 H, m, ArH),

7.25 (1 H, *J* 9 Hz, 1-H), 4.15 (2 H, d, aliph. H), 3.5 (4 H, t, morpholino), 3.1 (5 H, br s, aliph. H), 2.5 (1 H, s, aliph. H), and 1.95 (6 H, aliph. H) (Found: C, 63.8; H, 5.9; N, 9.8. $C_{22}H_{25}N_3O_3S$ requires C, 64.2; H, 6.1; N, 10.2%).

(*d*) The dichloro-2*H*-benzimidazole (**1**; $R^1 = R^2 = Cl$, $R^3 = H$) gave 2,3-*dichloro*-6H-*tetrahydroazepino*[1,2-a]*benzimidazole* (**21**) (75%), m.p. 176—177 °C; δ_H(60 MHz, $CDCl_3$) 7.7 (1 H, s, 4-H), 7.3 (1 H, 1-H), 4.1 (2 H, d, aliph. H), 3.0 (2 H, d, aliph. H), and 1.85 (6 H, s, aliph. H) (Found: C, 56.3; H, 4.9; N, 11.0. $C_{12}H_{12}Cl_2N_2$ requires C, 56.5; H, 4.7; N, 11%).

(*e*) The mixture of isomers (**5**) and (**6**) ($R = MeC_6H_5SO_2$) obtained from the 5-*p*-tolylsulphonyl-2*H*-benzimidazole had m.p. 176—185 °C; $\nu_{max.}$ 1 310 and 1 150 cm^{-1} (SO_2); δ_H(90 MHz, $CDCl_3$) 8.3 (d, *J* 2 Hz, 4-H) [*cf.* (**6**; $R = SO_2C_6H_5Me$)], 8.0—7.7 (m, ArH), 7.4—7.1 (m, ArH), 4.2 (2 H, d, aliph. H), 3.1 (2 H, d, aliph. H), 2.35 (3 H, s, Me), and 1.9 (6 H, br s, aliph. H) (Found: C, 66.6; H, 6.1; N, 8.1. $C_{13}H_{16}N_2O_2S$ requires C, 67.1; H, 6.0; N, 8.2%).

(*f*) The isomeric mixture from the methylsulphonyl-2*H*-benzimidazole (**4**; $R = MeSO_2$) had m.p. 140—155 °C; $\nu_{max.}$ 1 300 and 1 150 cm^{-1} (SO_2); δ_H($CDCl_3$) 8.25 (d, *J* 2 Hz, 4-H) [*cf.* (**6**; $R = SO_2Me$)], 8.0 [s, 1-H in (**5**)], 7.8 (m, benzimidazole H), 7.4 [d, *J* 9 Hz, 3-H in (**5**)], 4.25 (2 H, d, aliph. H), 3.1 (5 H, m, aliph. H), and 1.9 (6 H, s, aliph. H) (Found: C, 59.2; H, 6.1; N, 10.55. $C_{13}H_{16}N_2O_2S$ requires C, 59.1; H, 6.1; N, 10.6%).

(*g*) Thermolysis of 4-amino-5-ethoxycarbonyl-2*H*-benzimidazole (**17**) (5.0 g) in *o*-dichlorobenzene (10 ml) gave, when the product mixture was chromatographed over SiO_2 with light petroleum–ethyl acetate, as the first band a mixture of the 1-amino (**19**) and the 4-amino isomers (**20**). The second fluorescent band was 1-*amino*-2-*ethoxycarbonyl*-6H-*tetrahydroazepino*[1,2-a]*benzimidazole* (**19**) (3.7 g, 74%), m.p. 133—135 °C; $\nu_{max.}$ 3 380 and 3 260 (NH_2) and 1 670 cm^{-1} (C=O); δ_H(90 MHz, $CDCl_3$) 7.8 (d, *J* 9 Hz, H_b), 7.0 (d, *J* 9 Hz, H_a), 5.95 (2 H, br s, NH_2 exch. in D_2O), 4.6—4.2 (4 H, m, aliph. H), 3.0 (2 H, br d, aliph. H), 2.0—1.6 (6 H, br s, aliph. H), and 1.4 (3 H, t, *J* 7 Hz, OCH_2CH_3) (Found: C, 66.4; H, 7.0; N, 14.8. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%). Its formyl derivative (**19**; R = CHO) obtained (90%) from formic acid (98%) under reflux had m.p. 162—163 °C; $\nu_{max.}$ 3 260 (NH) and 1 700 cm^{-1} (C=O); δ_H(90 MHz, $CDCl_3$) 9.85 (1 H exch. D_2O, br s, NH), 8.5 (1 H, s, CHO), 7.85 (d, *J* 9 Hz, H_a), 7.5 (d, *J* 9 Hz, H_a), 4.5—4.1 (4 H, m, aliph. H), 3.05 (2 H, br s, aliph. H), 2.0—1.6 (6 H, br s, aliph. H), and 1.35 (3 H, t, *J* 7 Hz, OCH_2CH_3) (Found: C, 64.0; H, 6.4; N, 14.0. $C_{16}H_{19}N_3O_3$ requires C, 63.8; H, 6.4; N, 14.0%). By formylating the isomeric mixture (*cf.* above) and chromatographing the crude product over SiO_2 with light petroleum–ethyl acetate as eluant the first band gave 4-*amino*-3-*ethoxycarbonyl*-4-*formamido*-6H-*tetrahydroazepino*[1,2-a]*benzimidazole* (**20**; R = CHO) (64%), m.p. 171—172 °C; $\nu_{max.}$ 3 280 (NH) and 1 690 and 1 660 cm^{-1} (CO); δ_H(90 MHz, $CDCl_3$) 11.0 (1 H, br d, *J* 10 Hz, D_2O exch., NHCHO), 10.45 (1 H, d, *J* 10 Hz, D_2O exch., NHCHO), 7.9 (d, *J* 9 Hz, 1-H_b), 6.9 (d, *J* 9 Hz, H_a), 4.4 (2 H, q, *J* 7 Hz, OCH_2CH_3), 4.15 (2 H, br d, aliph. H), 3.05 (2 H, br d, aliph. H), 2.1—1.6 (6 H, br s, aliph. H), and 1.4 (3 H, t, *J* 7 Hz, OCH_2CH_3) (Found: C, 63.9; H, 6.35; N, 13.85. $C_{16}H_{19}N_3O_3$ requires C, 63.8; H, 6.35; N, 13.9%). The second band gave the isomeric formyl derivative (**19**) (*cf.* above).

(*h*) 5-Phenoxy-2*H*-benzimidazole[2] (**4**; R = PhO) (2.0 g), when heated to 170 °C under nitrogen for 0.5 h, gave a dark solid. This was dissolved in chloroform and purified on Al_2O_3 with light petroleum–ethyl acetate (5:1) as eluant. The brown oil thus obtained was further purified by flash chromatography (SiO_2) with diethyl ether to give a white solid, m.p. 110—120 °C [isomeric mixture (**5**) and (**6**) (R = PhO)]; δ_H($CDCl_3$) 7.65 [d, 4-H in (**5**) $J_{3,4}$ 9 Hz], 7.45—6.9 (m, ArH), 4.1 (2 H, br d, NCH_2), 3.05 (2 H, br d, CH_2), and 2.0—1.6 (6 H, br, aliph. H) (Found: C, 77.4; H, 6.6; N, 10.2. $C_{18}H_{18}N_2O$ requires C, 77.7; H, 6.5; N, 10.1%); *m/z* 278 (M^+).

(*i*) Thermolysis of the methylcyclohexane-2*H*-benzimidazoles (**25**). The 2′-methyl-2*H*-benzimidazole-2-spirocyclohexane (**25**; $R^1 = Me$, $R^2 = R^3 = H$) gave only the *methylhexahydroazepinobenzimidazole* (**26**) (Found: C, 77.6; H, 8.35; N, 13.8) The 3′-methyl isomer (**25**; $R^2 = Me$, $R^1 = R^3 = H$) when heated dry on an oil-bath (170 °C) gave an isomeric mixture (**27**; $R^1 = Me$, $R^2 = R^3 = H$ and $R^3 = Me$, $R^1 = R^2 = H$); δ_H(60 MHz, $CDCl_3$) 7.30 (4 H, m, ArH), 3.90 (2 H, m, CH_2), 2.88 (2 H, m, CH_2), 1.50 (5 H, m, aliph. H), and 0.85 (3 H, dd, 2 overlapping Me groups) (Found: C, 78.1; H, 7.95; N, 13.75). The 4′-methyl isomer (**25**; $R^3 = Me$, $R^1 = R^2 = H$) gave the *methyltetrahydrodroazepinobenzimidazole* (**27**; $R^2 = Me$, $R^1 = R^3 = H$); δ_H(60 MHz, $CDCl_3$) 7.32 (4 H, m, ArH), 4.10 and 3.08 (2 H, m, 2 CH_2), 1.45 (5 H, m, aliph. H), and 0.90 (d, *J* 7 Hz, Me) (Found: C, 77.8; H, 8.25; N, 13.8. $C_{13}H_{16}N_2$ requires C, 77.9; H, 8.05; N, 14.0%).

(*j*) Pyrolysis of the dispiro[benzimidazole-cyclohexane-benzimidazole] (**28**) gave the *bisbenzimidazodiazocine* (**29**) (Found: C, 74.65; H, 5.2; N, 19.0. $C_{18}H_{16}N_4$ requires C, 74.9; H, 5.6; N, 19.4%).

(*k*) The isobenzimidazole-2-spiro-2′-adamantane melted at 143 °C and resolidified on further heating. The first band eluted (Al_2O_3, benzene–ethyl acetate) was starting material (1%) and the second was the *benzimidazoazatricycloundecane* (**32**); δ_H(60 MHz, $CDCl_3$) 7.68 (1 H, m ArH), 7.15 (3 H, m, ArH), 4.55 (1 H, m, methine), 3.50 (1 H, m, methine), and 1.90 (12 H, m, aliph. H) (Found: C, 80.5; H, 7.45; N, 11.5. $C_{16}H_{18}N_2$ requires C, 80.7; H, 7.6; N, 11.8%).

(*l*) 2,2-Diphenyl-2*H*-benzimidazole (**11**) was prepared by refluxing *o*-phenylenediamine (4.0 g) and benzophenone (6.76 g) in dichlorobenzene (20 ml) for 2 h in a Dean and Stark apparatus. The mono-Schiff's base[10] was obtained, after driving off the solvent, as yellow crystals (9 g, 50%), m.p. 94—95.5 °C. To its solution in benzene (2 g in 100 ml) was added activated MnO_2 (20 g) and the mixture was stirred for 24 h. The suspension was filtered and the filtrate evaporated to dryness. Chromatography of the residue (Al_2O_3, C_6H_6) gave as the first fraction 2,2-*diphenyl*-2H-*benzimidazole* (**11**) (0.85 g, 43%), m.p. 157 °C; $\nu_{max.}$ 1 540 cm^{-1} (C=N); δ_H($CDCl_3$) 8—6.5 (ArH) (Found: C, 84.5; H, 5.6; N, 10.4. $C_{19}H_{14}N_2$ requires C, 84.4; H, 5.2; N, 10.4%). On melting the crystals, 1,2-diphenylbenzimidazole (**13**) was obtained (8%; m.p. 111—112 °C, lit.,[11] m.p. 112—113 °C).

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