Synthesis of 1*H*-1-Benzazepines by Thermolysis of 2a,7b-Dihydro-3*H*-cyclobut[*b*]indoles

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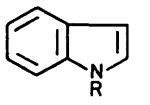
Syntheses and thermolyses of 3-substituted 2a,7b-dihydro-3*H*-cyclobut[*b*]indoles and some 2a-methyl derivatives are described. *X*-Ray crystal-structure analyses were carried out on the 3-acetyl and 3-pivaloyl derivatives, which both crystallise in the monoclinic system; space group $C2/c$, $Z = 8$, $a = 15.277(7)$, $b = 9.035(5)$, $c = 14.485(11)$ Å, $\beta = 104.27(5)°$ for the former, and space group $P2_1/c$, $Z = 4$, $a = 8.696(7)$, $b = 15.227(12)$, $c = 9.428(8)$ Å, $\beta = 102.67(7)°$ for the latter. The crystal structures were solved by direct methods, and atomic parameters refined to $R = 0.118$ (for the acetyl derivative) and $R = 0.108$ (for the pivaloyl derivative). No abnormal results were found. Direct thermolysis of the dihydrocyclobut[*b*]indoles resulted in the formation of 1-substituted 1*H*-1-benzazepines, *N*-substituted 1-naphthylamines, and 1-substituted indoles, whose relative distributions depend upon the nature of the substrate and the reaction temperature. The presence of silver ion significantly lowered the temperature necessary for ring opening and gave the 1*H*-1-benzazepines in variable yields. The 3-benzoyl-2a-methyl derivative, when heated in the presence of silver ion, gave both the rearrangement product 1-methyl dihydro-3*H*-cyclobut[*b*]indole and its ring-opened derivative, in addition to the 2-methyl-1*H*-1-benzazepine. The thermal and photochemical behaviour of these 1*H*-1-benzazepines is also described.

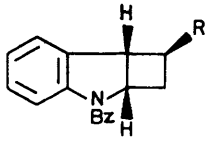
WHEREAS the chemistry of 1*H*-azepines [1] and dibenz[*b,f*]-azepines [2] has been studied to a considerable extent, that of 1*H*-1-benzazepines [3] remains relatively unexplored. In particular, only two examples of the derivatives lacking ring substituents are recorded in the literature [3a,b] and none of their chemistry has been reported. We now report the syntheses of 1*H*-1-benzazepines by the thermal ring-opening of 2a,7b-dihydro-3*H*-cyclobut[*b*]-indoles.[4]

Synthesis of Dihydro-3H-*cyclobut*[b]*indoles.*—Although there are two synthetic methods for the dihydro-3*H*-cyclobut[*b*]indoles (7) available,[3b,5] we now describe a more convenient synthesis of (7) starting from readily accessible 1-benzoylindole (1a). By applying the method of Jurian and Foster,[6] the photoadduct was obtained in 67% yield from (1a) and methyl acrylate as a mixture of stereoisomers. Several recrystallisations of the crude mixture gave a single major photoadduct, whose structure was assigned as methyl *cis-exo*-3-benzoyl-1,2,2a,7b-tetrahydro-3*H*-cyclobut[*b*]indole-1-carboxylate (2) by chemical correlation with *cis-exo*-3-benzoyl-1-hydroxy-1,2,2a,7b-tetrahydro-3*H*-cyclobut[*b*]indole (6).[7] Thus, mild alkaline hydrolysis of (2) with sodium hydroxide in aqueous methanol gave the carboxylic acid (3). Re-esterification of (3) with diazomethane in ether gave back (2), implying that no epimerisation took place during the alkaline hydrolysis step. The carboxylic acid (3) was treated with thionyl chloride followed by dimethylcadmium in ether to give the 1-acetyl derivative (4). Baeyer–Villiger oxidation of (4) with *m*-chloroperbenzoic acid (MCPBA) afforded the *exo*-1-acetoxy-derivative (5) which was identical with an authentic sample prepared from the known *exo*-alcohol (6).

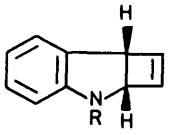
Oxidative decarboxylation of the carboxylic acid (3) with lead tetra-acetate in pyridine in the presence of copper(II) acetate [8] gave the desired cyclobutene (7a) in 26% yield. Lithium aluminium hydride reduction of (7a) in ether at room temperature afforded a mixture of



(1) a; R = Bz
b; R = Ac
c; R = COPr^i
d; R = COC_6H_{11}
e; R = COBu^t
f; R = CH_2Ph



(2) R = CO_2Me
(3) R = CO_2H
(4) R = Ac
(5) R = OAc
(6) R = OH

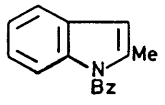


(7) a; R = Bz
b; R = Ac
c; R = COPr^i
d; R = COC_6H_{11}
e; R = COBu^t
f; R = CH_2Ph

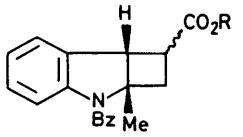
[(8) R = H]

the amine (8) and the 3-benzyl derivative (7f) in a *ca.* 2 : 1 ratio. Because of the instability of (8), the crude mixture was directly treated with acetic anhydride, isobutyryl chloride, cyclohexanecarbonyl chloride, or pivaloyl chloride to give the corresponding 3-acyl derivatives (7b—e), respectively, in 42—58% yield, together with (7f) (*ca.* 16—24%). The 3-benzyl derivative (7f) was also obtained in 80% yield by benzylation of the mixture of (8) and (7f) with benzyl bromide. The same sequence of reactions starting from 1-benzoyl-2-methylindole (9) gave the 2a-methyl derivative (12).

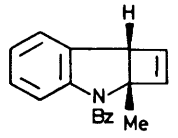
The structures of these cyclobutenes were apparent from their spectral data. The mass spectra of the cyclobutenes (7a—f) showed the molecular-ion peak (*a*) and two diagnostically important fragment ions (*b*) and



(9)

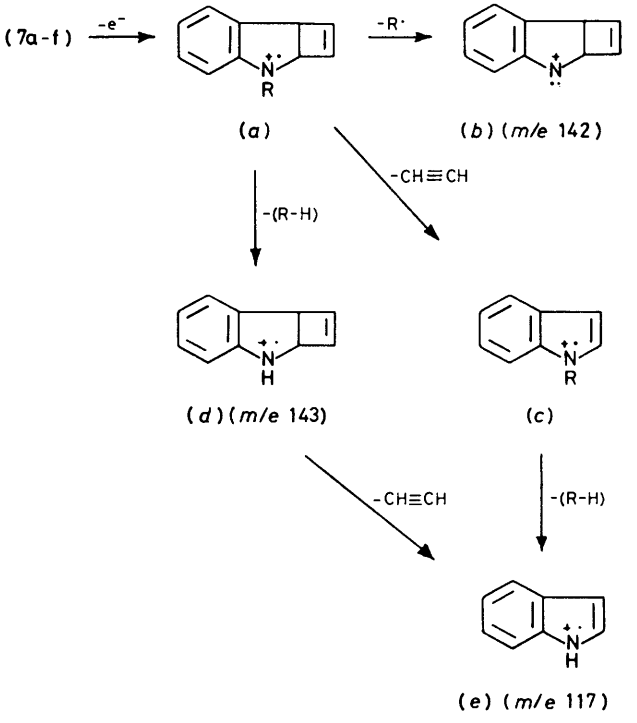


(10) R = Me
(11) R = H



(12)

(*c*). In the case of compounds (7b—e) the additional ion peaks (*d*) and (*e*) were observed (Scheme 1). The n.m.r. spectra were well resolved and the chemical shifts and coupling constants are recorded in the Experimental section.



SCHEME 1

Crystal Structures.—The *X*-ray crystal-structure analyses were carried out on the 3-acetyl (7b) and 3-pivaloyl (7e) derivatives. The molecular structures of (7b) and (7e) are illustrated in the Figure. No significant differences in bond lengths or angles (Tables 1 and 2) between (7b) and (7e) were observed.

Thermolysis.—We are particularly interested in the possibility of rearranging the dihydro-3*H*-cyclobut[*b*]-

TABLE 1

Bond distances (Å) and bond angles (°) involving non-hydrogen atoms with estimated standard deviations in parentheses for compound (7b)

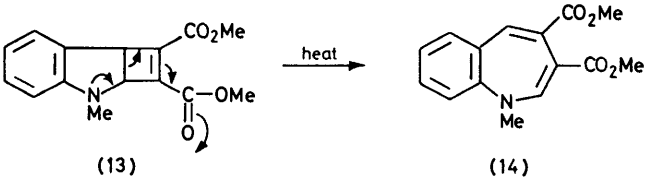
C(1)–C(2)	1.31(1)	C(1)–C(7B)	1.55(1)
C(2)–C(2A)	1.52(1)	C(2A)–C(7B)	1.56(1)
C(2A)–N(3)	1.50(1)	N(3)–C(9)	1.44(1)
N(3)–C(10)	1.38(1)	C(4)–C(9)	1.38(1)
C(4)–C(5)	1.40(1)	C(5)–C(6)	1.35(1)
C(6)–C(7)	1.38(1)	C(7)–C(8)	1.40(1)
C(8)–C(7B)	1.51(1)	C(8)–C(9)	1.40(1)
O–C(10)	1.21(1)	C(10)–C(11)	1.54(1)
C(2)–C(1)–C(7B)	94.9(7)	C(1)–C(2)–C(2A)	94.7(7)
N(3)–C(2A)–C(2)	115.3(7)	N(3)–C(2A)–C(7B)	104.8(6)
C(2)–C(2A)–C(7B)	86.3(6)	C(2A)–N(3)–C(9)	109.6(6)
C(2A)–N(3)–C(10)	125.9(7)	C(9)–N(3)–C(10)	124.3(7)
C(5)–C(4)–C(9)	116.7(7)	C(4)–C(5)–C(6)	123.0(8)
C(5)–C(6)–C(7)	120.1(9)	C(6)–C(7)–C(8)	119.5(8)
C(1)–C(7B)–C(2A)	84.0(6)	C(1)–C(7B)–C(8)	114.1(7)
C(2A)–C(7B)–C(8)	104.5(7)	C(7)–C(8)–C(7B)	130.4(8)
C(7)–C(8)–C(9)	118.9(8)	C(7B)–C(8)–C(9)	110.7(7)
N(3)–C(9)–C(4)	128.1(7)	N(3)–C(9)–C(8)	110.1(7)
C(4)–C(9)–C(8)	121.7(7)	O–C(10)–N(3)	123.2(8)
O–C(10)–C(11)	123.7(8)	N(3)–C(10)–C(11)	113.1(7)

TABLE 2

Bond distances (Å) and bond angles (°) involving non-hydrogen atoms with estimated standard deviations in parentheses for compound (7e)

C(1)–C(2)	1.311(8)	C(1)–C(7B)	1.521(8)
C(2)–C(2A)	1.533(8)	C(2A)–C(7B)	1.576(7)
C(2A)–N(3)	1.492(7)	N(3)–C(9)	1.436(6)
N(3)–C(10)	1.371(7)	C(4)–C(9)	1.391(7)
C(4)–C(5)	1.387(7)	C(5)–C(6)	1.371(8)
C(6)–C(7)	1.388(8)	C(7)–C(8)	1.373(7)
C(8)–C(7B)	1.506(7)	C(8)–C(9)	1.409(7)
O–C(10)	1.223(6)	C(10)–C(11)	1.550(7)
C(11)–C(12)	1.517(8)	C(11)–C(13)	1.553(8)
C(11)–C(14)	1.552(8)		
C(2)–C(1)–C(7B)	95.8(5)	C(1)–C(2)–C(2A)	94.1(5)
N(3)–C(2A)–C(2)	116.8(4)	N(3)–C(2A)–C(7B)	106.8(4)
C(2)–C(2A)–C(7B)	85.3(4)	C(2A)–N(3)–C(9)	108.1(4)
C(2A)–N(3)–C(10)	127.6(4)	C(9)–N(3)–C(10)	123.7(4)
C(5)–C(4)–C(9)	117.1(5)	C(4)–C(5)–C(6)	122.0(5)
C(5)–C(6)–C(7)	120.8(5)	C(6)–C(7)–C(8)	118.8(5)
C(1)–C(7B)–C(2A)	84.7(4)	C(1)–C(7B)–C(8)	113.8(5)
C(2A)–C(7B)–C(8)	102.5(4)	C(7)–C(8)–C(7B)	128.4(5)
C(7)–C(8)–C(9)	120.3(5)	C(7B)–C(8)–C(9)	111.3(4)
N(3)–C(9)–C(4)	128.3(5)	N(3)–C(9)–C(8)	110.6(4)
C(4)–C(9)–C(8)	121.0(5)	O–C(10)–N(3)	120.6(5)
O–C(10)–C(11)	118.6(5)	N(3)–C(10)–C(11)	120.8(4)
C(10)–C(11)–C(12)	108.1(4)	C(10)–C(11)–C(13)	106.1(4)
C(10)–C(11)–C(14)	113.7(4)	C(12)–C(11)–C(13)	110.5(5)
C(12)–C(11)–C(14)	112.0(5)	C(13)–C(11)–C(14)	106.4(5)

indoles to their valence isomers, 1*H*-1-benzazepines. There are many examples of this type of transformation,[3c,f-i,k-m] but all of them involve ring expansion of the cyclobutene derivatives obtained by cycloaddition of 1-alkyl- or 3-amino-indoles with acetylenic esters [*e.g.* (13) ⟶ (14)]. Such a ring-opening reaction takes place with relative ease because the electron-donor and -acceptor are substituted at the appropriate positions.[9]



(13) (14)

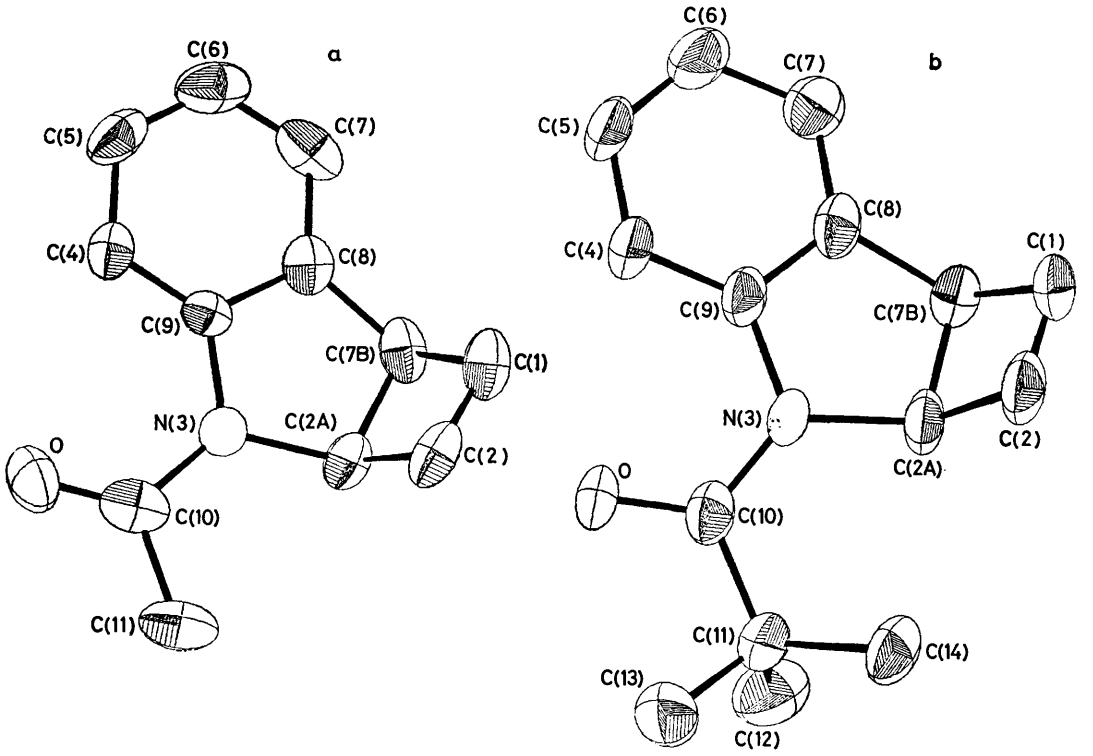


FIGURE Perspective ORTEP drawings of (a) compound (7b) and (b) compound (7e). Each atom is represented by the following thermal ellipsoids for clarity: carbon atom, boundary and principal ellipses with octant shading; nitrogen atom, boundary ellipse only; oxygen atom, boundary and principal ellipses

In contrast to the case of (13), the ring-opening reaction of the dihydro-3*H*-cyclobut[*b*]indoles (7a—f) required much higher temperatures. Thus, when heated at 270—280 °C for 10 min in the absence of solvent, (7a) gave 1-benzoyl-1*H*-1-benzazepine (15a) (major product) and *N*-benzoyl-1-naphthylamine (16a) (minor product) as an inseparable mixture (total 73%), along with 1-benzoylindole (1a) (4%) and unchanged (7a) (23%). At higher temperatures (300—310 °C) (7a) gave (16a) as the major product. Similar conversions of (7b—e) into the corresponding 1*H*-1-benzazepines (15b—e) and other products was accomplished in yields listed in Table 3. The 2a-methyl congener (12) also underwent a ring-opening reaction at 250 °C to give exclusively 2-methyl-1*H*-1-benzazepine (18) in 92% yield. The structural assignments of these 1*H*-1-benzazepines were based on their spectroscopic data (i.r., u.v., mass, and ^{1}H n.m.r.) and the catalytic hydrogenation of (15a) over platinum oxide to 1-benzoyl-2,3,4,5-tetrahydro-1*H*-1-benzazepine (17).[10]

TABLE 3

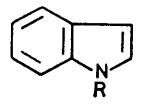
Product distribution from thermolyses of dihydro-3*H*-cyclobut[*b*]indoles

Compound	Conditions	Isolated yields (%) (15) [or (18)]	(16)	(1)	(7) [or (12)]
(7a)	270—280 °C, 10 min	73 [a]	*a*	4	23
(7a)	300—310 °C, 3 min	0	90	Trace	0
(7b)	320 °C, 10 min	43	0	3	45
(7c)	270—280 °C, 10 min	62 [a]	*a*	Trace	23
(7d)	270—280 °C, 10 min	58	Trace	Trace	36
(7e)	230 °C, 10 min	27	0	0	71
(7e)	250 °C, 10 min	73	Trace	Trace	16
(7e)	270—280 °C, 10 min	6	57	Trace	18
(7f)	Refluxing xylene, 10 min	88	0	0	0
(12)	230 °C, 10 min	20 [b]	0	0	65 [c]
(12)	250 °C, 20 min	92 [b]	0	0	0

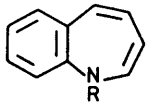
[a] Obtained as an inseparable mixture containing a small amount of (16). [b] Compound (18). [c] Compound (12).

Although detailed mechanistic studies were not carried out, the intermediacy of biradicals (A) seems most plausible in view of the elevated temperatures required for this reaction and the general acceptance of biradicals in the related thermal ring opening of fused cyclobutenes.[11] One aspect of the ring-opening reaction

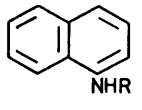
is that the more bulky the 3-acyl group of (7), the lower the temperature necessary for the reaction. It would be of interest to know the precise structures of these cyclobutenes in order to relate them to the observed



(1a-f)



(15a-f)

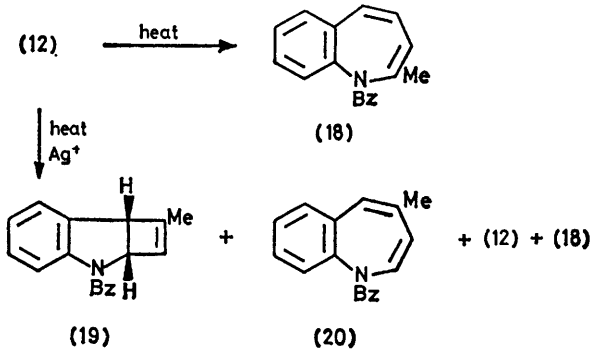


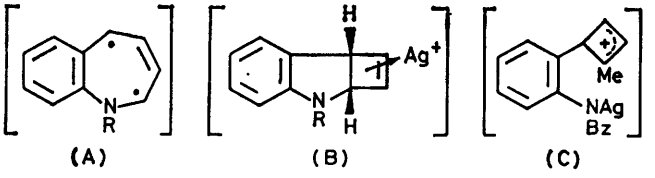
(16a-f)

(17)

a; R = Bz b; R = Ac c; R = $COPr^i$
d; R = COC_6H_{11} e; R = $COBu^t$ f; R = CH_2Ph

reactivity, and thus the conformations of the cyclobutenes (7b) and (7e) have been determined by *X*-ray analyses. However, as mentioned earlier, there are no significant differences in either the bond lengths or angles between the two cyclobutenes and thus the difference in the temperature necessary for ring-opening cannot be attributed, at least, to the different conformations of these





SCHEME 2

molecules in the ground state. The formation of the naphthylamine derivatives will be discussed later.

In contrast, the 3-benzyl derivative (7f) underwent smooth ring opening at a much lower temperature (140 °C). A thermally allowed disrotatory ring-opening process of the five-membered heterocyclic ring may be operating in this case.

Interestingly, the temperature for ring-opening of (7a—e) was found to be lowered by up to 100—160 °C in the presence of silver ion. Thus, refluxing a solution of (7a) in xylene in the presence of silver tetrafluoroborate for 10 h gave (15a) (58%) and the starting material (7a) (34%) (Table 4). No reaction took place in the absence of silver ion at this temperature. Prolonged heating (20 h) did not change the product ratio, suggesting the reversibility of the reaction, since treatment of (15a) under the same conditions also gave a mixture of (7a) and (15a).

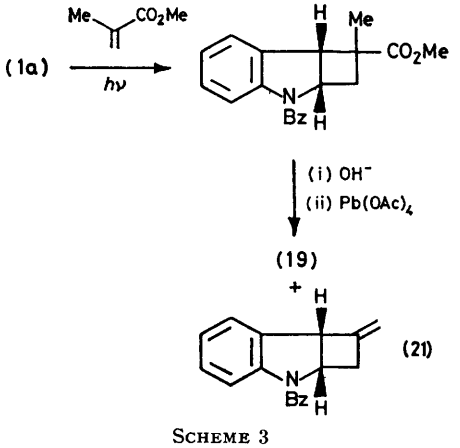
TABLE 4

Silver ion-catalysed thermolysis of dihydro-3*H*-cyclobut[*b*]indoles

Compound	Conditions	Isolated yields (%) (15)	(7)
(7a)	Refluxing xylene, 10 h	58	34
(7b)	Refluxing mesitylene, 5 h	18	72
(7c)	Refluxing xylene, 5 h	43	49
(7d)	Refluxing xylene, 5 h	43	39
(7e)	Refluxing xylene, 5 h	12	63

Similar results were obtained for (7b—e) (Table 4). Interestingly, treatment of the 2a-methyl derivative (12) with silver tetrafluoroborate gave a mixture of the rearranged cyclobutene (19) (43%), the 1*H*-1-benzazepine (20) (4%), the 1*H*-1-benzazepine (18) (8%), and starting cyclobutene (12) (43%) (Scheme 2). The structure assignment of compound (19) * was based on spectral evidence and its conversion into the benzazepine (20).

The silver ion-catalysed ring-opening reaction of the



SCHEME 3

cyclobutenes may be a result of the complexation of the cyclobutene double bond to silver ion [see (B), Scheme 2].[12] The rearrangement of (12) to (19) would involve heterolytic cleavage of the C(2a)–N bond to give an intermediate (C), followed by recombination in an alternative manner.

Physical Properties of 1H-1-*Benzazepines*.—The u.v. spectra of the 1-acyl-1*H*-benzazepines (15a—e) show two major absorption maxima comprising a high-intensity

* Attempted synthesis of (19) by the route shown in Scheme 3 resulted in the formation of an inseparable mixture of (19) and (21) in a ratio of 1 : 2 (unpublished results).

band at 209—230 nm and a broad band of medium intensity at 260—290 nm. The absorption maxima of the 1-benzyl derivative (15f) appear at 209 and 250 nm.

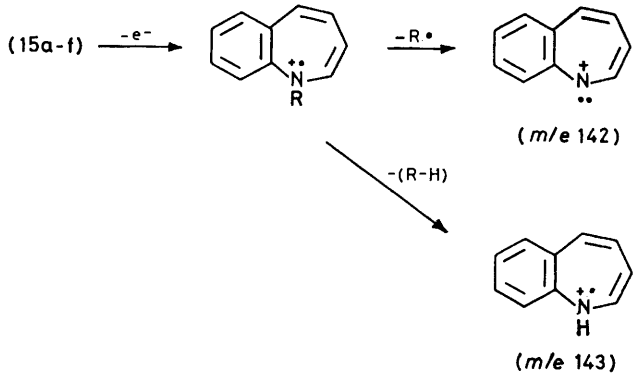
The n.m.r. spectra of the 1*H*-1-benzazepines are listed in Table 5. The assignments of these signals were based on the coupling patterns and comparisons with the n.m.r. spectra of (18) and (20) as well as those of benzoxepin [13] and benzothiepin.[14] The chemical shifts (δ) of the ring protons of the 1-acyl-1*H*-1-benzazepines (15a—e) appear in the order of 3-H > 4-H > 2-H > 5-H. In the n.m.r. spectrum of the 1-benzyl derivative (15f), the signals of the ring protons, in particular the 2-H and 3-H proton signals, are shifted upfield.

TABLE 5

^{1}H N.m.r. spectral data (δ values) for 1*H*-1-benzazepines (*J* values in Hz)

Compd.	H-2	H-3	H-4	H-5	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	Aromatic	Others
(15a)	6.72 (d)	5.97 (dd)	6.41 (dd)	7.02 (d)	8.0	5.5	12.0	6.7—7.4 (9 H, m)	
(15b)	6.49 (d)	5.91 (dd)	6.24 (dd)	6.84 (d)	7.5	6.0	11.0	6.9—7.5 (4 H, m)	1.82, 2.19 (total 3 H, 2 × s)
(15c)	6.53br (d)	5.97 (dd)	6.33 (dd)	6.93 (d)	7.5	5.5	11.0	6.7—7.5 (4 H, m)	0.83, 1.16 (total 6 H, 2 × d, *J* 7 Hz) 2.2—3.2 (1 H, m)
(15d)	6.52 (d)	5.95 (dd)	6.31 (dd)	6.92 (d)	7.5	5.5	11.5	6.8—7.6 (4 H, m)	0.6—2.9br (11 H)
(15e)	6.63 (d)	5.96 (dd)	6.36 (dd)	7.04 (d)	8.0	5.0	11.5	7.1—7.4 (4 H, m)	1.18 (9 H, s)
(15f)	5.46 (d)	5.10 (dd)	5.96 (dd)	6.59 (d)	7.5	5.5	11.0	6.6—7.6 (9 H, m)	4.41 (2 H, s)
(18)	—	5 96 (d)	6.42 (dd)	7.07 (d)	—	6.0	11.0	6.7—7.4 (9 H, m)	2.12 (3 H, s)
(20)	6.70 (d)	5.80 (d)	—	6.77 (s)	8.0	—	—	6.9—7.2 (9 H, m)	2.09 (3 H, s)

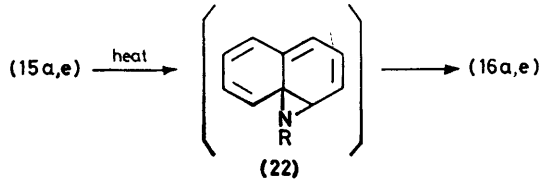
The mass spectra of the 1*H*-1-benzazepines (15a—f) show a formal similarity to that of the corresponding 2a,7b-dihydrocyclobut[*b*]indoles (7a—f) except for the $[M - CH{\equiv}CH]^+$ and *m/e* 117 ion peaks which are very weak or absent in the former (Scheme 4).



SCHEME 4

Thermal and Photochemical Behaviour of 1H-1-*Benzazepines.*—Compound (15a) when heated at 300—310 °C for 3 min in the absence of solvent gave *N*-benzoyl-1-naphthylamine (16a) in 90% yield. Interestingly, the pivaloyl derivative (15e) rearranged at lower temperature (270 °C) to give (16e) in 77% yield The observed rearrangement is analogous to that of substituted *N*-methoxycarbonylazepines [15] and is rationalised in terms of 1a*H*-naphth[1,8a-*b*]azirine intermediates (22) which may arise *via* an electrocyclic reaction. The 2-methyl derivative (18) was thermally stable and was recovered unchanged after being heated at 280 °C for 10 min; at 310 °C several new compounds were formed (t.l.c.) but no characterisable products could be isolated.

Irradiation of compound (15a) in tetrahydrofuran for 4 h under argon gave (7a) in 81% yield. Similarly, compound (15c) was transformed into (7c) in 73% yield. This photochemical valence-tautomerism closely parallels the behaviour of 1-benzoxepin [5] and 1-benzothiepin.[14] The same isomerisation has been observed with substituted 1*H*-1-benzazepines.[3k,l] The 2-methyl derivative (18) also isomerised [to (12)] but the reaction was very slow (25% conversion after irradiation for 21 h).



EXPERIMENTAL

N.m.r. spectra were determined with an Hitachi R-22 spectrometer (90 MHz; $SiMe_4$ as internal standard). I.r. spectra were recorded with a JASCO IRA-1 spectrophotometer and u.v. spectra with an Hitachi 124 spectrophotometer. Low- and high-resolution mass spectra were recorded with Hitachi RMU-6D and JMS-D-300 instruments, respectively, at 70 eV. Irradiations were carried out using an Eikosha 350 W high-pressure mercury lamp with a Pyrex filter.

Methyl cis-exo-3-*Benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (2).—(*a*) *From* (1a). According to the procedure reported by Jurian and Foster,[6] a degassed solution of the amide (1a) [16] (8.0 g) and methyl acrylate (15 ml) in benzene (500 ml) was irradiated under nitrogen for 30 h. After the solvent had been evaporated off, the residue was chromatographed on silica gel [n-hexane–ethyl acetate [4 : 1)] to give the adducts (7.4 g, 67%) as an oily mixture of stereoisomers which was crystallised from n-hexane. Three recrystallisations from n-hexane–AcOEt gave a single isomer (2) of the *ester*, m.p. 109.5—110 °C (Found: C, 74.35; H, 5.5; N, 4.85. $C_{19}H_{17}NO_3$ requires C, 74.25; H, 5.58; N, 4.56%); $\nu_{max.}$ ($CHCl_3$) 1 725 and 1 630 cm^{-1}; δ($CDCl_3$) 2.5—2.8 (2 H, m), 3.0—3.25 (1 H, m), 3.70 (3 H, s, OMe), 4.05—4.25 (1 H, m), 4.6—4.9 (1 H, m), 6.9—7.5 (8 H, m, aromatic), and 7.8—8.2br (1 H, 4-H).

(*b*) *From* (3). To a solution of compound (3) (*vide infra*) (200 mg) in ethanol (3 ml) and ether (5 ml) was added

a solution of a large excess of diazomethane in ether at room temperature, and the mixture was kept for 2 h. The excess of diazomethane and the solvent were removed under reduced pressure and the residue was recrystallised from n-hexane–ethyl acetate to give (2) (170 mg, 81%), m.p. 109.5—110 °C.

cis-exo-3-*Benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylic Acid* (3).—A mixture of the ester (2) (1.9 g), sodium hydroxide (300 mg), and water (1 ml) in ethanol (30 ml) was stirred at 50 °C for 1 h. After the solvent had been evaporated off, the residue was dissolved in water and the solution acidified with 10% aqueous hydrochloric acid. The precipitated crystals were collected, washed with water, and dried to give the *acid* (3) (1.6 g, 88%), m.p. 218—220 °C (from ethanol) (Found: C, 73.8; H, 5.1; N, 4.8. $C_{18}H_{15}NO_3$ requires C, 73.70; H, 5.15; N, 4.78%); $\nu_{max.}$ (KCl) 2 500—3 300, 1 735, and 1 630 cm^{-1}.

cis-exo-1-*Acetyl*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (4).—A mixture of the acid (3) (150 mg) and thionyl chloride (1 ml) was refluxed for 30 min. The excess of thionyl chloride was evaporated off and the residue was dissolved in anhydrous ether (5 ml). To the solution was added, dropwise, an ethereal solution of dimethylcadmium [prepared from methylmagnesium bromide (0.13 mmol) and cadmium chloride (117 mg, 0.64 mmol)]. The mixture was stirred at room temperature for 4 h and poured into ice–water. The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (n-hexane–ethyl acetate, 7 : 1) to give the *ketone* (4) (81 mg, 55%), m.p. 112—113 °C (from benzene–n-hexane) (Found: C, 78.1; H, 5.85; N, 5.0. $C_{19}H_{17}NO_2$ requires C, 78.33; H, 5.88; N, 4.81%); $\nu_{max.}$ (KCl) 1 690 and 1 640 cm^{-1}; $\delta(CDCl_3)$ 2.17 (3 H, s, COMe), 2.45—2.7 (2 H, m), 3.1—3.8 (1 H, m), 4.1—4.3 (1 H, m), 4.62 (1 H, q, *J* 7 Hz), 7.0—7.5 (8 H, m, aromatic), and 7.8—8.25br (1 H, 4-H).

cis-exo-1-*Acetoxy*-3-*benzoyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole* (5).—(*a*) *From* (4). A mixture of the ketone (4) (150 mg, 0.52 mmol) and MCPBA (98 mg, 0.57 mmol) in methylene dichloride (7 ml) was kept at room temperature overnight. The reaction mixture was washed with 10% aqueous sodium carbonate and water, dried ($MgSO_4$), and concentrated to give the *ester* (5) (146 mg, 92%), m.p. 93.5—95 °C (from n-hexane–ethyl acetate) (Found: C, 74.35; H, 5.5; N, 4.75. $C_{19}H_{17}NO_3$ requires C, 74.25; H, 5.58; N, 4.56%); $\nu_{max.}$ ($CHCl_3$) 1 725 and 1 635 cm^{-1}; $\delta(CDCl_3)$ 1.92 (3 H, s, COMe), 2.25—2.6 (1 H, m), 2.7—3.05 (1 H, m), 4.2—4.5 (2 H, m), 4.9—5.2 (1 H, m), 6.9—7.5 (8 H, m, aromatic), and 7.8—8.2br (1 H, 4-H).

(*b*) *From* (6). A mixture of the alcohol (6) [7] (100 mg), acetic anhydride (2 ml), and pyridine (2 ml) was kept at room temperature overnight. The reaction mixture was diluted with water and extracted with ether. The extract was washed with 10% aqueous sodium carbonate and brine, dried ($MgSO_4$), and concentrated to give a solid which was recrystallised from n-hexane–ethyl acetate giving (5) (101 mg, 87%).

cis-3-*Benzoyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indole* (7a).—To a solution of the acid (3) (1.47 g, 5 mmol) in dry benzene (50 ml) and pyridine (130 mg) was added copper(II) acetate (100 mg) and then lead tetra-acetate (4.43 g, 10 mmol). The mixture was refluxed under nitrogen for 1 h. After cooling, ethylene glycol (5 ml) was added and the mixture was washed with water, 10% aqueous nitric acid, water, 10% aqueous sodium hydroxide, water, and brine, and then dried ($MgSO_4$) and concentrated. The residual solid was recrystallised from propan-2-ol to give the *cyclobutene* (7a) (326 mg, 26%), m.p. 190—191 °C (Found: C, 82.3; H, 5.3; N, 5.75. $C_{17}H_{13}NO$ requires C, 82.57; H, 5.30; N, 5.66%); $\nu_{max.}$ (KCl) 1 640 cm^{-1}; $\delta(CDCl_3)$ 4.35br (1 H, d, *J* 4 Hz, 7b-H), 5.00 (1 H, br. d, *J* 4 Hz, 2a-H), 6.07 (1 H, dd, *J* 3 and 1.5 Hz, 2-H), 6.42 (1 H, dd, *J* 3 and 1 Hz, 1-H), and 6.9—7.65 (8 H, m, aromatic); *m/e* 247 (M^+, 13%), 221 (7), 142 (8), and 105 (100).

cis-3-*Benzyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indole* (7f).—A mixture of compound (7a) (200 mg, 0.81 mmol) and lithium aluminium hydride (62 mg) in anhydrous ether (8 ml) was stirred at room temperature for 15 min. The excess of hydride was decomposed by addition of water and the inorganic material was dissolved in a saturated Rochelle salt solution. The organic layer was separated, washed with brine, dried ($MgSO_4$), and concentrated. The residue was dissolved in methylene dichloride (5 ml) and benzyl bromide (103 mg) was added. After being kept at room temperature overnight, the mixture was washed with 10% aqueous sodium carbonate, dried ($MgSO_4$), and concentrated. The residue was chromatographed on alumina [n-hexane–ethyl acetate (10 : 1)] to give the *tertiary amine* (7f) (152 mg, 80%) as an oil (Found: *m/e* 233.1213. $C_{17}H_{15}N$ requires *M*, 233.1205); $\delta(CDCl_3)$ 4.15—4.5 (3 H, m, PhCH_2 and 7b-H), 4.58 (1 H, dd, *J* 4 and 2 Hz, 2a-H), 5.86 (1 H, dd, *J* 3 and 2 Hz, 2-H), 6.31 (1 H, dd, *J* 3 and 1 Hz, 1-H), and 6.35—7.35 (9 H, m, aromatic); *m/e* 233 (M^+, 24%), 207 (45), 142 (100), 115 (20), and 91 (77).

cis-3-*Acetyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indole* (7b).—The reaction mixture obtained by lithium aluminium hydride reduction of (7a) (124 mg) was dissolved in acetic anhydride (5 ml) and the mixture was kept at room temperature for 1 h and concentrated. The residue was dissolved in chloroform and the solution was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. The residue was chromatographed on alumina. Elution with n-hexane–ethyl acetate (10 : 1) gave the amine (7f) (28 mg, 24%). Further elution with the same solvent gave the acetamide (7b) (135 mg, 52%), m.p. 94—95 °C (from n-hexane) (lit.,[5] 94—95 °C); $\nu_{max.}$ (KCl) 1 650 cm^{-1}; $\delta(CDCl_3)$ 2.22 (3 H, s, COMe), 4.40 (1 H, br. d, *J* 4 Hz, 7b-H), 5.05 (1 H, dd, *J* 4 and 2 Hz, 2a-H), 6.13br (1 H, d, *J* 2 Hz, 2-H), 6.42 (1 H, dd, *J* 4 and 1 Hz, 1-H), 6.35—7.3 (3 H, m, aromatic), and 8.22 (1 H, m, 4-H); *m/e* 185 (M^+, 36%), 159 (18), 143 (43), 142 (25), and 117 (100).

cis-3-*Isobutyryl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indole* (7c).—The reaction mixture obtained by lithium aluminium hydride reduction of (7a) (300 mg) was dissolved in pyridine (5 ml) and isobutyryl chloride (116 mg) was added. The mixture was kept at room temperature overnight, poured into ice–water, and extracted with chloroform. The extract was washed with 10% aqueous hydrochloric acid, water, saturated aqueous sodium hydrogencarbonate, and water, and then dried ($MgSO_4$) and concentrated. The residue was chromatographed on alumina. Elution with n-hexane–ethyl acetate (9 : 1) gave the amine (7f) (71 mg, 24%). Further elution with the same solvent gave the *isobutyramide* (7c) (135 mg, 52%), m.p. 114.5—115 °C (from n-hexane) (Found: C, 79.0; H, 7.1; N, 6.6. $C_{14}H_{15}NO$ requires C, 78.84; H, 7.09; N, 6.57%); $\nu_{max.}$ (KCl) 1 640 cm^{-1}; $\delta(CDCl_3)$ 1.24 [6 H, d, *J* 6 Hz, CHMe_2], 2.76 [1 H, septet, *J* 6 Hz, C*H*Me_2], 4.42 (1 H, dd, *J* 4.5 and 2 Hz, 7b-H), 5.18 (1 H, dd, *J* 4.5 and 1.5 Hz, 2a-H), 6.16 (1 H, dd,

J 3 and 1.5 Hz, 2-H), 6.47 (1 H, dd, *J* 3 and 2 Hz, 1-H), 6.85—7.4 (3 H, m, aromatic), and 8.30br (1 H, d, 4-H); *m/e* 213 (M^+, 32%), 187 (8), 143 (87), 142 (26), and 117 (100).

cis-3-*Cyclohexylcarbonyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]-*indole* (7d).—The reaction mixture obtained by lithium aluminium hydride reduction of (7a) (300 mg) was treated with cyclohexanecarbonyl chloride (160 mg) in pyridine (5 ml) at room temperature. Work-up as previously described gave the amine (7f) (48 mg, 16%) and the *amide* (7d) (179 mg, 58%), m.p. 95—96.5 °C (from n-hexane) (Found: C, 80.6; H, 7.5; N, 5.6. $C_{17}H_{19}NO$ requires C, 80.57; H, 7.56; N, 5.53%); $\nu_{max.}$ (KCl) 1 645 cm^{-1}; δ($CDCl_3$) 0.8—2.7 (11 H, m), 4.42br (1 H, d, *J* 4 Hz, 7b-H), 5.19br (1 H, d, *J* 2.5 Hz, 2a-H). 6.17br (1 H, d, *J* 1.5 Hz, 2-H), 6.45br (1 H, 1-H), 6.8—7.4 (3 H, m, aromatic), and 8.32br (1 H, d, 4-H); *m/e* 253 (M^+, 19%), 227 (4), 143 (100), 142 (11), and 117 (61).

cis-3-*Pivaloyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]*indole* (7e).—The reaction mixture obtained by lithium aluminium hydride reduction of (7a) (150 mg) was treated with pivaloyl chloride (60 mg) in pyridine (3 ml) and work-up gave the amine (7f) (27 mg, 18%) and the *amide* (7e) (58 mg, 42%), m.p. 143—144 °C (from n-hexane) (Found: C, 79.2; H, 7.6; N, 6.1. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%); $\nu_{max.}$ (KCl) 1 640 cm^{-1}; δ($CDCl_3$) 1.39 (9 H, s, CMe_3), 4.44 (1 H, d, *J* 3 Hz, 7b-H), 5.44 (1 H, dd, *J* 3 and 1 Hz, 2a-H), 6.09 (1 H, dd, *J* 3 and 1.5 Hz, 2-H), 6.50 (1 H, dd, *J* 3 and 1 Hz, 1-H), 6.8—7.4 (3 H, m, aromatic), and 8.27 (1 H, m, 4-H); *m/e* 227 (M^+, 26%), 201 (12), 143 (32), 142 (18), 117 (44), and 57 (100).

1-*Benzoyl*-2-*methylindole* (9).—Essentially, the procedure of Illi [16] was employed for the benzoylation step. To an ice-cooled mixture of 2-methylindole (20.2 g, 0.15 mol), tetrabutylammonium hydrogen sulphate (1.0 g), and powdered sodium hydroxide (15.0 g, 0.375 mol) in methylene dichloride (1.5 l) was added a solution of benzoyl chloride (23.0 g, 0.163 mol) in methylene dichloride (50 ml) during 0.5 h. After being stirred at room temperature for 2 h, the mixture was filtered and the filtrate concentrated. In order to remove the unchanged 2-methylindole, the residue was treated with 40% aqueous dimethylamine (12 ml) and 30% formalin (8 ml) in acetic acid (14 ml) at room temperature for 1 h. The precipitated solid was recrystallised from ethanol to give the *indole* (9) (18.4 g, 51%), m.p. 74—74.5 °C (Found: C, 81.75; H, 5.5; N, 6.15. $C_{16}H_{13}NO$ requires C, 81.68; H, 5.57; N, 5.95%); $\nu_{max.}$ (KCl) 1 680 cm^{-1}; δ($CDCl_3$) 2.36 (3 H, s, Me), 6.34 (1 H, s, 3-H), and 6.8—7.8 (9 H, m, aromatic).

Methyl cis-3-*Benzoyl*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylate* (10).—Using a similar procedure to that described for the preparation of (2), the photoadduct (7.06 g, 51%) was obtained as a *ca.* 10 : 1 mixture of two stereoisomers (n.m.r. spectroscopy) by irradiation of a mixture of compound (9) (10.1 g) and methyl acrylate (35 ml) in benzene (500 ml) for 83 h. One recrystallisation of the crude mixture from n-hexane gave a single isomer (10) of the *ester*, m.p. 122 °C (Found: C, 74.9; H, 5.9; N, 4.5. $C_{20}H_{19}NO_3$ requires C, 74.74; H, 5.96; N, 4.36%); $\nu_{max.}$ (KCl) 1 745 and 1 650 cm^{-1}; δ($CDCl_3$) 1.70 (3 H, s, 2a-Me), 2.5—3.3 (3 H, m, 1-H and 2-H_2), 3.76 (4 H, s, OMe and 7b-H), 6.2—6.4 (1 H, m, 4-H), and 6.8—7.6 (8 H, m, aromatic).

cis-3-*Benzoyl*-2a-*methyl*-1,2,2a,7b-*tetrahydro*-3H-*cyclobut*[b]*indole*-1-*carboxylic Acid* (11).—Using a similar procedure to that described for the preparation of (3), *compound* (11) (800 mg, 84%) was obtained from the ester (10) (1.0 g), and had m.p. 233 °C (from ethanol) (Found: C, 73.9; H, 5.4; N, 4.7. $C_{19}H_{17}NO_3$ requires C, 74.25; H, 5.58; N, 4.56%); $\nu_{max.}$ (KCl) 2 500—3 000, 1 720, and 1 605 cm^{-1}.

cis-3-*Benzoyl*-2a-*methyl*-2a,7b-*dihydro*-3H-*cyclobut*[b]-*indole* (12).—Using a similar procedure to that described for the preparation of (7a), the *cyclobutene* (12) (1.39 g, 34%) was obtained from the acid (11) (4.80 g), and had m.p. 152 °C (from propan-2-ol) (Found: C, 82.8; H, 5.6; N, 5.3. $C_{18}H_{15}NO$ requires C, 82.73; H, 5.79; N, 5.36%); $\nu_{max.}$ (KCl) 1 630 cm^{-1}; δ($CDCl_3$) 1.70 (3 H, s, 2a-Me), 3.93 (1 H, d, *J* 1 Hz, 7b-H), 6.34 (1 H, dd, *J* 3 and 1 Hz, 2-H), 6.46 (1 H, d, *J* 3 Hz, 1-H), 6.5—6.8 (1 H, m, 4-H), and 6.85—7.6 (8 H, m, aromatic); *m/e* 261 (M^+, 7%), 235 (10), 156 (22), and 105 (100).

X-*Ray Analyses of Compounds* (7b) *and* (7e).—*Crystal data.* Compound (7b), $C_{12}H_{11}NO$, M = 185.2. Monoclinic, a = 15.277(7), b = 9.035(5), c = 14.485(11) Å, β = 104.27(5)°, U = 1937.7 Å^3, Z = 8, D_c = 1.27 g cm^{-3}. Space group $C2/c$. μ(Mo-K_α) = 0.9 cm^{-1}. Compound (7e), $C_{15}H_{17}NO$, M = 227.3. Monoclinic, a = 8.696(7), b = 15.227(12), c = 9.428(8) Å, β = 102.67(7)°, U = 1218.0 Å^3, Z = 4, D_c = 1.24 g cm^{-3}. Space group $P2_1c$. μ(Mo-K_α) = 0.8 cm^{-1}.

Data collection. A crystal was mounted on a Syntex R_3 four-circle automated diffractometer. The cell dimensions were refined by least-squares using 23 [for (7b)] and 19 [for (7e)] reflections measured on the diffractometer with graphite-monochromated Mo-K_α radiation. Intensity data were collected on the diffractometer with the same radiation using an ω–2θ scanning technique with 2θ < 45° [for (7b)] and 60° [for (7e)]. Three reference reflections monitored periodically showed no significant intensity fluctuations during the course of the data collection. A total of 1 103 [for (7b)] and 2 123 [for (7e)] reflections were used for the structure analyses. Intensities were corrected for Lorentz and polarisation factors, but not for absorption.

Structure determination and refinement. The structure was solved by direct methods (MULTAN [17]). The positional co-ordinates were refined by block-diagonal least-squares, using anisotropic temperature factors for all non-hydrogen atoms and isotropic ones for hydrogen atoms. The determined temperature factors of the hydrogen atoms of the methyl group in (7b) were abnormally high, probably due to disorder. The final R-values were 0.118 [for (7b)] and 0.108 [for (7e)]. The atomic scattering factors were taken from ref. 18. Bond lengths and angles are listed in Tables 1 and 2. Observed and calculated structure factors, atomic co-ordinates, and thermal parameters are listed in a Supplementary publication [SUP No. 23230 (27 pages)].*

General Procedure for Thermolysis of Cyclobutenes (7a—f) *and* (12).—(*a*) *Direct thermolysis.* A cyclobutene (7a—e) or (12) (100 mg) in a flask was heated in the absence of solvent at the appropriate temperature (determined by heating a sample in a capillary tube) on a preheated metal bath for 10—20 min. After cooling, the reaction mixture was chromatographed on alumina [n-hexane–ethyl acetate (6 : 1)]. In the case of the 3-benzyl derivative (7f), xylene was used as solvent: after refluxing for 10 min, the mixture was concentrated and the residue was passed through a short alumina column (n-hexane). The reaction temper-

* For details of the Supplementary Publications scheme, see Notice to Authors No 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

ature and product distributions are summarised in Table 3.

(*b*) *Thermolysis in the presence of silver ion.* A mixture of a cyclobutene (7a—e) or (12) (100 mg) and silver tetrafluoroborate (100 mg) in xylene (7 ml) was refluxed for 10 h. The organic layer was washed with water, dried ($MgSO_4$), and concentrated. The residue was submitted to column chromatography on alumina [n-hexane–ethyl acetate (6 : 1)]. The results are summarised in Table 4. The products obtained were as follows (^1H n.m.r. data given in Table 5). 1-*Benzoyl*-1H-1-*benzazepine* (15a), oil (Found: *m/e* 247.0982. $C_{17}H_{13}NO$ requires *M*, 247.0969); $\nu_{max.}$ (film) 1 650 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 222 and 280 nm (log ε 4.26 and 3.73); *m/e* 247 (M^+, 28%), 142 (28), 115 (16), and 105 (100). 1-*Acetyl*-1H-1-*benzazepine* (15b) was an oil (Found: *m/e* 185.0813. $C_{12}H_{11}NO$ requires *M*, 185.0787); $\nu_{max.}$ ($CHCl_3$) 1 650 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 230 and 280 nm (log ε 3.69 and 3.21); *m/e* 185 (M^+, 28%), 143 (100), and 142 (39). 1-*Isobutyryl*-1H-1-*benzazepine* (15c) was an oil (Found: *m/e* 213.1169. $C_{14}H_{15}NO$ requires *M*, 213.1153); $\nu_{max.}$ (film) 1 660 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 228 and 279 nm (log ε 4.14 and 3.60); *m/e* 213 (M^+, 11%), 143 (100), and 142 (45) 1-*Cyclohexylcarbonyl*-1H-1-*benzazepine* (15d) was an oil (Found: *m/e* 253.1486. $C_{17}H_{19}NO$ requires *M*, 253.1506); $\nu_{max.}$ (film) 1 665 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 228 and 279 nm (log ε 4.08 and 3.57); *m/e* 253 (M^+, 5%), 143 (100), and 142 (7). 1-*Pivaloyl*-1H-1-*benzazepine* (15e) had m.p. 94—95 °C (from n-hexane) (Found: *m/e* 227.1306. $C_{15}H_{17}NO$ requires *M*, 227.1304); $\nu_{max.}$ (KCl) 1 650 cm^{-1}; $\lambda_{max.}$ (EtOH) (end absorption) 225 and 274 nm (log ε 4.15 and 3.68); *m/e* 227 (M^+, 25%), 143 (63), 142 (63), and 57 (100). 1-*Benzyl*-1H-1-*benzazepine* (15f), was an oil (Found: *m/e* 233.1200. $C_{17}H_{15}N$ requires *M*, 233.1202); $\lambda_{max.}$ (EtOH) 209 and 250 nm (log ε 3.95 and 3.51); *m/e* 233 (M^+, 17%), 142 (100), 115 (21), and 91 (10). 1-*Benzoyl*-2-*methyl*-1H-1-*benzazepine* (18) had m.p. 107—108 °C (from n-hexane) (Found: C, 82.85; H, 5.6; N, 5.5. $C_{18}H_{15}NO$ requires C, 82.73; H, 5.79; N, 5.39%); $\nu_{max.}$ (KCl) 1 625 cm^{-1}; $\lambda_{max.}$ (EtOH) 209, 267, and 288 nm (log ε 4.52, 4.04, and 3.91); *m/e* 261 (M^+, 30%), 156 (86), and 105 (100). cis-3-*Benzoyl*-1-*methyl*-2a,7b-*dihydrocyclobut*[b]*indole* (19) had m.p. 133 °C (from ethyl acetate) (Found: C, 82.8; H, 5.7; N, 5.45. $C_{18}H_{15}NO$ requires C, 82.73; H, 5.79; N, 5.39%); $\nu_{max.}$ (KCl) 1 635 cm^{-1}; δ($CDCl_3$) 1.74 (3 H, s, 1-Me), 4.18br (1 H, d, *J* 4 Hz, 7b-H), 4.84br (1 H, 2a-H), 5.79br (1 H, d, *J* 1 Hz, 2-H), 6.9—7.6 (8 H, m, aromatic), and 7.8—8.2 (1 H, m, 4-H); *m/e* 261 (M^+, 7%), 221 (4), 156 (21), and 105 (100). 1-*Benzoyl*-4-*methyl*-1H-1-*benzazepine* (20) was an oil (Found: *m/e* 261.1154. $C_{18}H_{15}NO$ requires *M*, 261.1154); $\nu_{max.}$ (KCl) 1 620 cm^{-1}; *m/e* 261 (M^+, 40%), 156 (66), and 105 (100).

Catalytic Hydrogenation of Compound (15a).—A solution of compound (15a) (132 mg) in ethanol (2 ml) was hydrogenated over platinum oxide (20 mg) at room temperature for 8 h. The mixture was filtered and the filtrate was concentrated to give 1-benzoyl-2,3,4,5-tetrahydro-1*H*-1-benzazepine (17) (62 mg, 47%), m.p. 86—87 °C (from n-hexane) (lit.,[10] 85—86 °C).

Thermal Isomerisation of Compounds (15a) *and* (15e).—A sample of compound (15a) (21 mg) was heated at 300—310 °C for 10 min. The residue was recrystallised from n-hexane to give *N*-benzoyl-1-naphthylamine (16a) (18 mg, 90%), m.p. 161 °C (lit.,[19] 161 °C). Similarly, compound (15e) (90 mg) was heated at 270 °C for 5 min, and the residue was chromatographed on alumina [n-hexane–ethyl acetate (6 : 1)] to give N-*pivaloyl*-1-*naphthylamine* (16e) (69 mg, 77%) and unchanged compound (15e) (10 mg, 12%). Compound (16e) had m.p. 150—151 °C (from n-hexane–ethyl acetate) (Found: C, 79.35; H, 7.55; N, 6.15. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%); $\nu_{max.}$ (KCl) 3 240, 1 640, and 1 500 cm^{-1}; δ($CDCl_3$) 1.30 (9 H, s, 3 × Me) and 7.1—7.9 (7 H, m, aromatic). No NH signal was detected. This compound was identical (m.p., i.r., and n.m.r. spectra) with an authentic sample prepared from 1-naphthylamine and pivaloyl chloride.

Photochemical Isomerisation of Compounds (15a), (15c), *and* (18).—A solution of compound (15a) (120 mg) in anhydrous tetrahydrofuran (12 ml) was irradiated for 4 h under argon. The mixture was evaporated to dryness and the residue was passed through a short alumina column [n-hexane–ethyl acetate (9 : 1)] to give (7a) (97 mg, 81%). Similarly, compound (15c) (80 mg) isomerised to (7c) (58 mg, 73%). Irradiation of the benzazepine (18) for a period of 21 h gave a mixture of (12) and (18) in a ratio of *ca.* 1 : 3 (n.m.r. spectroscopy).

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