Azonia-azulenes. Part 6.[1] Photochemical Addition of Alcohols to 10*H*-Azepino[1,2-*a*]indoles

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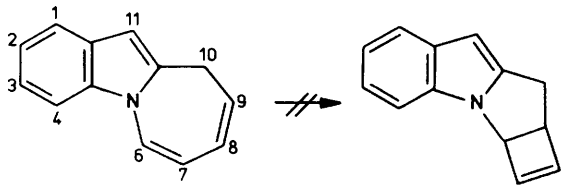
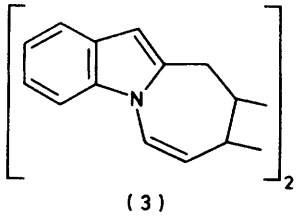
Irradiation of solutions of the azepinoindole (1) in methanol or ethanol gives the 6- and 9-alkoxy-6,9-dihydroazepinoindoles (5), (24), (4), and (23); the other major products are the benzo[*b*]cyclobuta[*hi*]indolizines (6) and (25). Other substituted azepinoindoles (7)—(10) give correspondingly substituted methanol addition products. The 8-methylazepinoindole (9) also gives an 8,9-dihydro-8-methoxyazepinoindole (18), and the 7,9-dimethylazepinoindole (10) gives a 6,7-dihydro-7-methoxyazepinoindole (22). A mechanism is proposed for these reactions, and some confirmatory evidence provided by the irradiation of the azepinoindole (1) in methan[^{2}H]-ol. The azepinoindoles (9) and (10) were synthesized by decomposition of the corresponding *o*-azido-phenylmethylbenzene.

We have used intramolecular nitrene insertion reactions to obtain a wide variety of new heterocyclic systems.[2-8] One of the most consistently successful of these insertions used *o*-azido-phenylmethylbenzene to produce azepino-[1,2-*a*]indoles, a reaction first reported [9] as giving 11*H*-azepino[1,2-*a*]indoles. We have shown that the products are 10*H*-azepino[1,2-*a*]indoles, the parent having the structure (1). Such compounds can be obtained in substantial quantities, and we have started to evaluate these 10*H*-azepinoindoles as potential starting materials for the production of other heterocycles. We report here their behaviour when irradiated in solutions in alcohols. We have used the azepinoindole (1),[2] the dideuterio-derivative (7),[6] and the 11-methyl- (8),[2] 8-methyl- (9), and 7,9-dimethyl- (10) azepinoindoles. The last two compounds are new, and were synthesized by standard methods.



(1) (2)

(7) 10,11-$^2H_2$
(8) 11-Me
(9) 8-Me
(10) 7,9-Me_2



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Our own work on the photochemistry of annelated tropones [10,11] and many literature reports on the photochemistry of cycloheptadienes,[12] cycloheptatrienes,[13] and benzocycloheptadienes [14] led us to expect, as a principal product, the tetracyclic compound (2). However, irradiation of a dilute solution of the azepinoindole (1) in methanol, using a medium-pressure mercury-lamp with a Pyrex sleeve, gave no product of type (2). The reaction was monitored by the decrease in intensity of the absorption maximum at 315 nm which had completely disappeared after 8 h. In subsequent preparative runs we chose to stop irradiation after 5—6 h, sacrificing some yield of the major product in exchange for a cleaner product mixture with recovery of some starting material. Separation of the mixture by chromatography on alumina gave four products, one of which was a photodimer, probably of structure (3), but present only in small amounts. The other three products were isomers of formula $C_{14}H_{15}NO$, formally derived from the azepinoindole (1) by addition of a molecule of methanol. These are shown below as 6,9-dihydro-9-methoxyazepinoindole (4) [type (A)], 6,9-dihydro-6-methoxyazepinoindole (5) [type (B)], and 1a,4,9b,10-tetrahydro-10-methoxybenzo[*b*]cyclobuta[*hi*]indolizine (6) [type (C)]. Similar

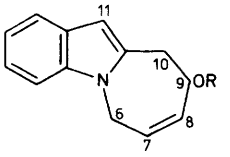
TABLE 1

Products obtained from azepinoindoles by photolysis in alcohols [a]

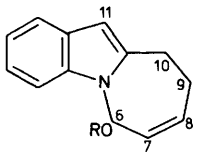
Azepinoindole	Alcohol	Type (A) [%]	Type (B) [%]	Type (C) [%]	Dimer [%]	Other products [%]
(1)	MeOH	(4) [24] [b]	(5) [5]	(6) [9.5]	*d*	
(1)	EtOH	(23) [27]	(24) [3]	(25) [9]	*d*	
(1)	Bu^{t}OH				Major [30]	
(1)	MeOD [c]	(27) [15]				(28)
(7; 10,11-$^2H_2$)	MeOH	(11) [23]	(15) [5]	(19) [7]	*d*	
(8; 11-Me)	MeOH	(12) [36]	(16) [2]	(20) [5]		
(9; 8-Me)	MeOH	(13) [11]	(17) [11]	(21) [11]		(18) [12]
(10; 7,9-Me_2)	MeOH	(14) [32]				(22) [26]

[a] 1 g in 500 ml of alcohol; 5—6 h irradiation. [b] Yield 57%, with decrease in Type (B) and (C). Maximum yield. [c] 0.5 g in 180 ml. [d] Some dimer produced.

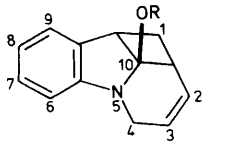
products have been obtained from the substituted azepindoindoles (7)—(10) (Table 1). The products of type (B) and (C) were unstable to p.l.c., giving poor recovery, so that not all of these were fully characterised by microanalysis, but all were obtained in sufficiently pure states to provide useful information *via* ^{1}H n.m.r. spectroscopy. Each type of adduct will be dealt with in turn, and the mechanism of the photoaddition discussed afterwards.



Type (A)
(4) R = Me
(11) R = Me; 10,11-$^2H_2$
(12) R = Me; 11-Me
(13) R = Me; 8-Me
(14) R = Me; 7,9-Me_2
(23) R = Et
(27) R = Me; 6-^{2}H



Type (B)
(5) R = Me
(15) R = Me; 10,11-$^2H_2$
(16) R = Me; 11-Me
(17) R = Me; 8-Me
(24) R = Et



Type (C)
(6) R = Me
(19) R = Me; 1,9b-$^2H_2$
(20) R = Me; 9b-Me
(21) R = Me; 2-Me
(25) R = Et

RESULTS

The major product from most of the photolyses [type (A)] had the same general structure as compound (4). The ^{1}H n.m.r. spectrum of the simplest compound, the methoxy-derivative (4), and data for all the compounds of this type are shown in Table 2. The most immediate observation is that a simple indole is present (11 H signal at δ 6.3), showing that methanol addition has occurred on the seven-membered ring. The multiplets at δ 5.2 and 5.7 are due to alkene protons, and the similarity of chemical shift makes it unlikely that they are attached to a double bond which is conjugated with the indole. The possible positions for the double bond are hence 7,8 or 8,9. From its chemical shift, the multiplet (2 H) at δ 3.9 is next to the nitrogen atom, and irradiation at δ 3.9 simplifies the alkene signals to a doublet (J 12 Hz) and a pair of doublets (J 14 and 2 Hz), so that the double bond can be placed at 7,8; the 12 Hz coupling is acceptable for a cycloheptene. A multiplet at δ 3.7 (1 H) can be shown to be due to 9-H, since irradiation at this position simplified the signal at δ 5.7 to a doublet, and revealed an eight-line signal at δ 5.47 (J 12, 3, and 6 Hz, 7-H). The only signal unassigned, a multiplet (2 H) at δ 3.05, must be due to 10- and 10′-H. The substituted compounds (11)—(14) provided confirmation of the structural assignments. Thus, the dideuterioazepinoindole (7) gave a type (A) product with a much reduced indole proton signal, and an integral for the multiplet at δ 2.9 of only one proton. The product (13) from the 8-methylazepinoindole (9) had a signal for only one alkene proton, a triplet, while the 9-H signal was also simplified to a triplet. The simplest spectrum was that of compound (14), where the single alkene signal is a broad singlet, coupled to one of the two signals δ 3.8 (dd) and 4.1 (d) due to 6- and 6′-H. There is no signal due to 9-H, and the greater conformational rigidity also produces a clear separation in the doublets due to 10- and 10′-H, at δ 2.95 and 3.2. The ^{13}C n.m.r. spectrum confirms the structure of compound (4); the signals in the aromatic region (5 × CH, 3 quaternary) at δ 136.6, 136, 128, 120.5, 120, 119, 108, and 100.4 p.p.m. agree well with those of 1,2-dimethylindole.[15] In the alicyclic–aliphatic region there are signals at δ 77 (C-9), 56 (OMe), 41.5 (C-6), and 30.5 (C-10) p.p.m., and the alkene signals are at δ 125 and 132.5 p.p.m.

The second class of compounds [type (B)] were the least stable, although both types (B) and (C) decomposed during p.l.c. and recovery from plates was very poor. Because of this instability only the most abundant of these compounds could be fully characterized by microanalysis. All, however, could be obtained pure (^{1}H n.m.r.) and all gave correct molecular ions on mass spectroscopy. Compound (5) showed, in its ^{1}H n.m.r. spectrum (Table 2) the multiplets at δ 7.5—7.6 (1 H) and 6.8—7.3 (3 H), and a subsplit singlet at δ 6.2, indicating an intact indole moiety. The signal from the methoxy-group was at very high field in [$^2H_6$]benzene (δ 2.8) but in a more normal position in deuteriochloroform (δ 3.2), indicating that the methoxy-group must be fairly close to the oriented benzene solvent-molecules. The three-proton multiplet at δ 5.5 was assigned to 6-, 7-, and 8-H, the extra downfield shift in 6-H compared with that in compound (4) being due to the substituent methoxy-group. The remaining signals were at δ 2.8, 2.5, and 2.0 and were all complex multiplets. Irradiation at δ 2.0 simplified the other multiplets, revealing one as a doublet (J 14 Hz) and the other as a subsplit doublet; irradiation at δ 6.2 removed the minor coupling at δ 2.8 and hence the latter signal must be due to 10-H, and that at δ 2.5 to 10′-H. Not all the azepinoindoles gave type (B) products, but those which did fully confirm the structure assigned (Table 2). From the 8-methylazepinoindole (9), an additional product was obtained in which the methyl group signal was a sharp singlet at δ 1.2. The characteristic indole pattern was interrupted by a doublet at δ 6.6 (J 11 Hz), coupled to a broadened doublet at δ 4.7; these two signals were assigned to the protons attached to a double bond conjugated with the nitrogen

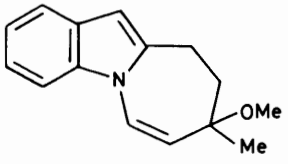
TABLE 2

^{1}H N.m.r. shifts [a] and coupling constants for 6- and 9-alkoxyazepinoindoles

Compd.	1—3-H	4-H	6-H	7-H	8-H	9-H	10-H	11-H	Other	*J* values (Hz)
(4)	7.1m	7.6m	3.9m	5.47m	5.74m	3.7m	3.0m	6.3s	3.1 (s, OMe)	$J_{6,7}$2.8; $J_{6',7}$6.3; $J_{7,8}$12; $J_{7,9}$1.7
(11)	7.1m	7.6m	3.9m	5.3m	5.4m	3.7m	3.0m [b]	6.3s [c]	3.1 (s, OMe)	$J_{7,8}$12
(12)	7.1m	7.6m	3.9m	5.4m	5.8m	3.7m	3.1m	2.2s	3.1 (s, OMe)	$J_{7,Me}$1.5; $J_{9,10}$6
(13)	7.1m	7.7m	4.0m	5.2t	1.65d	3.5t	2.95m	6.3s	3.05 (s, OMe)	$J_{6,6'}$14; $J_{6,8}$1.3; $J_{10,10'}$14
(14)	7.2m	7.7m	4.1d 3.8dd	1.55s	5.1br s	0.95s	3.2d 2.95d	6.25s	2.95 (s, OMe)	
(23)	7.1m	7.6m	3.9m	5.35m	5.7m	3.7m	2.9m	6.35s	1.05 (3 H, t, CH_2Me) 3.3 (2 H, dq, OCH_2)	
(27)	7.1m	7.6m	4.0m [d]	5.35qd	5.7br d	3.7m	2.9m	6.3s [d]	3.1 (s, OMe)	$J_{7,8}$12; $J_{6,7}$6.5; $J_{7,9}$1.7
(5)	7.1m	7.6m	←———	5.5m	———→	2.1m	2.8m	2.15d	2.85 (s, OMe)	$J_{10,10'}$14; $J_{10',11}$1
(15)	← 7.35m →		←———	5.9m	———→	2.4m	3.0m [d] 3.5m [d]		3.2 (s, OMe)	
(16) [e]	7.2m	7.6m	←———	5.7m	———→	2.1m	2.8m	2.15d	2.85 (s, OMe)	
(17)	7.2m	7.6m	← 5.6br s →		1.45s	1.9m	2.6dt 3.5m	6.25s	2.8 (s, OMe)	$J_{10',10}$14; $J_{10',11}$1; $J_{9,10'}$3.5; $J_{9,10}$8
(24)	← 7.3m →		←———	6.0br s	———→	3.3m	2.2m	6.3s	1.1 (3 H, t, CH_2Me) 3.2 (q, OCH_2)	

[a] Multiplet centres given in p.p.m. from $SiMe_4$; C_6D_6 solutions. [b] Integral = 1 H. [c] Integral = 0.3 H. [d] Integral = *ca.* 0.5 H. [e] Spectrum determined in $CDCl_3$.

atom of the indole system. A series of multiplets (4 H) lying between the methoxy-signal at δ 3.05 and the methyl signal at δ 1.2 could be assigned to 9-, 9′-, 10-, and 10′-H, and the total spectrum provides the evidence for structure (18). The formation of this apparently anomalous product is discussed later.



(18)

The third class of photo-product, type (C),* were structurally the most interesting, being due to a skeletal rearrangement. The first observation from the ^{1}H n.m.r. spectrum of compound (6) (Table 3) was that there is no signal at δ 6.2—6.3 due to the indole β-hydrogen, and the multiplet (4 H) in the aromatic region is now entirely upfield of the normal benzene position, indicating an aniline or indoline structure. Two alkene signals (each 1 H), at δ 5.3 and 5.6, shown by double irradiation to be coupled to the multiplet (2 H) at δ 3.6 and to the poorly resolved multiplet at δ 3.0, had a major coupling of 10 Hz, less than that observed for the seven-membered ring alkenes (4) and (5). The quartet at δ 3.35 (1 H) can be shown to be coupled to the multiplets at δ 2.3 and 1.2.

The absence of any signals at δ 3.35 in compounds (19) and (20), derived from an [11-^{2}H]- and an 11-methyl-azepindoindole respectively, show that this signal is due to the original β-indolic proton (11-H) in the azepino-indoles. Furthermore, reduced integrals for the signals at δ 2.3 and 1.2 in compound (19), derived from the [10,11-$^2H_2$]azepinoindole (7), place these as the original 10-protons, so that, during some rearrangement, a bond has been formed between C-10 and -11 of the azepino-indole. We thus have the sequence $-C(6)H_2{\cdot}C(7)H{=}C(8)H{\cdot}CH{\cdot}C(10)H_2{\cdot}C(11)H-$. The coupling constants, derived from the two 10-H multiplets, are in good agreement with those expected for a cyclobutane, and only satisfactory formula for type (C) compounds is as a benzo[*b*]cyclobuta[*h*,*i*]indolizine [as in formulae (6) and (19)—(21)]. The ^{13}C n.m.r. spectrum gave additional confirmation, with signals at δ 30 (C-10), 38.5 and 40 (C-9 and -11), 46 (C-6), 49 (OMe), 92 (C-9a), 107 (C-4), 117 (C-2), 123 and 123 (C-7 and -8), 127 and 127 (C-1 and -3), 135 (C-11a), and 152 p.p.m. (C-4a).

Two compounds were obtained from the 7,9-dimethyl-azepinoindole (10) with very similar ^{1}H n.m.r. spectra. The first was the type (A) compound, already described, and the second is the allylic isomer (22). The methyl group signals were at δ 1.1 (s) and 1.5 (d, *J* 1.5 Hz). A single alkene signal at δ 5.2 was shown by double irradiation to be coupled to the methyl group signal at δ 1.5 and to the upfield part of an AB pair of signals at δ 2.7 and 3.25 ($J_{A,B}$ 14 Hz). The other signals showed the normal indole pattern and the methoxy-group (δ 3.1), and there was a singlet (2 H) at δ 4.0 due to 6-H.

Two attempts have been made to extend the reaction by using other alcohols. Irradiation of the azepino-indole (1) in ethanol showed that the maximum at 315 nm disappeared at approximately the same rate as in methanol, but the residue after evaporation contained some polymer (n.m.r.). Separation of the products gave compounds (23)—(25). A mixture of t-butyl alcohol–benzene (4 : 1) as solvent for the azepinoindole (1) gave a

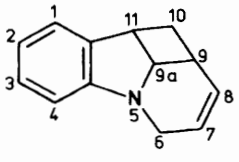
TABLE 3

^{1}H N.m.r. data for benzocyclobutaindolizines

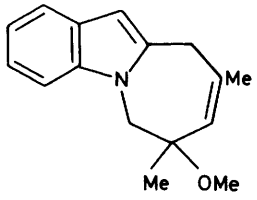
Compd.	1—4-H	6-H	7-H	8-H	9-H	10-H	11-H	Other	*J* values (Hz)
(6) [b]	7.05dt 6.9td 6.65dt 6.4d	3.6br s	5.35—5.4 m	5.6—5.35 m	2.95—3.05 m	2.25m 1.2m	3.35—3.4 q	3.1 (OMe)	$J_{9,10}$7; $J_{7,8}$10 $J_{10,10'}$11.5; $J_{9,10}$11 $J_{10',11}$5.3; $J_{10,11}$9.5
(19)	7.05dt 6.9td 6.65dt 6.4d	3.6br s	5.3—5.45 m	5.6—5.65 m	2.95—3.05 m	2.25m [c] 1.2m [c]		3.1 (OMe)	
(20)	7.05dt 6.9td 6.65dt 6.4d	3.6m	5.4m	5.7m	2.9—3.0 m	1.9t 1.30m	1.45 (S, Me)	3.1 (OMe)	$J_{7,8}$10; $J_{10,10'}$11.2; $J_{10,10'}$11.2
(21)	7.05st 6.9t 6.65dt 6.4d	3.6m	5.1m	1.35 (q, Me)	2.95—3.05 m	2.3m 1.25m	3.4q	3.1(OMe)	$J_{9,10'}$6.5; $J_{9,10}$11 $J_{10,11}$9.5; $J_{10',11}$5.0 $J_{10,10'}$11.2
(25)	7.05d 6.9t 6.65dt 6.4d	3.58m	5.3m	5.65m	3.0m	2.25m 1.2m	3.3m	3.3 (q, OCH_2) 1.1 (t, CH_2*Me*)	$J_{7,8}$10; $J_{7,9}$2; $J_{8,9}$4; $J_{10,11}$9.5; $J_{10',10}$11; $J_{9,10}$11

[a] Chemical shifts (δ) are in p.p.m. from TMS. [b] 300 MHz. [c] Integrating for 0.5 H each.

* The systematic numbering for compounds of type (C) is as shown and has been used in naming these compounds. However, for simplicity, the numbering of the original azepinoindoles (shown below) has been retained for the ^{1}H and ^{13}C n.m.r. spectral assignments.



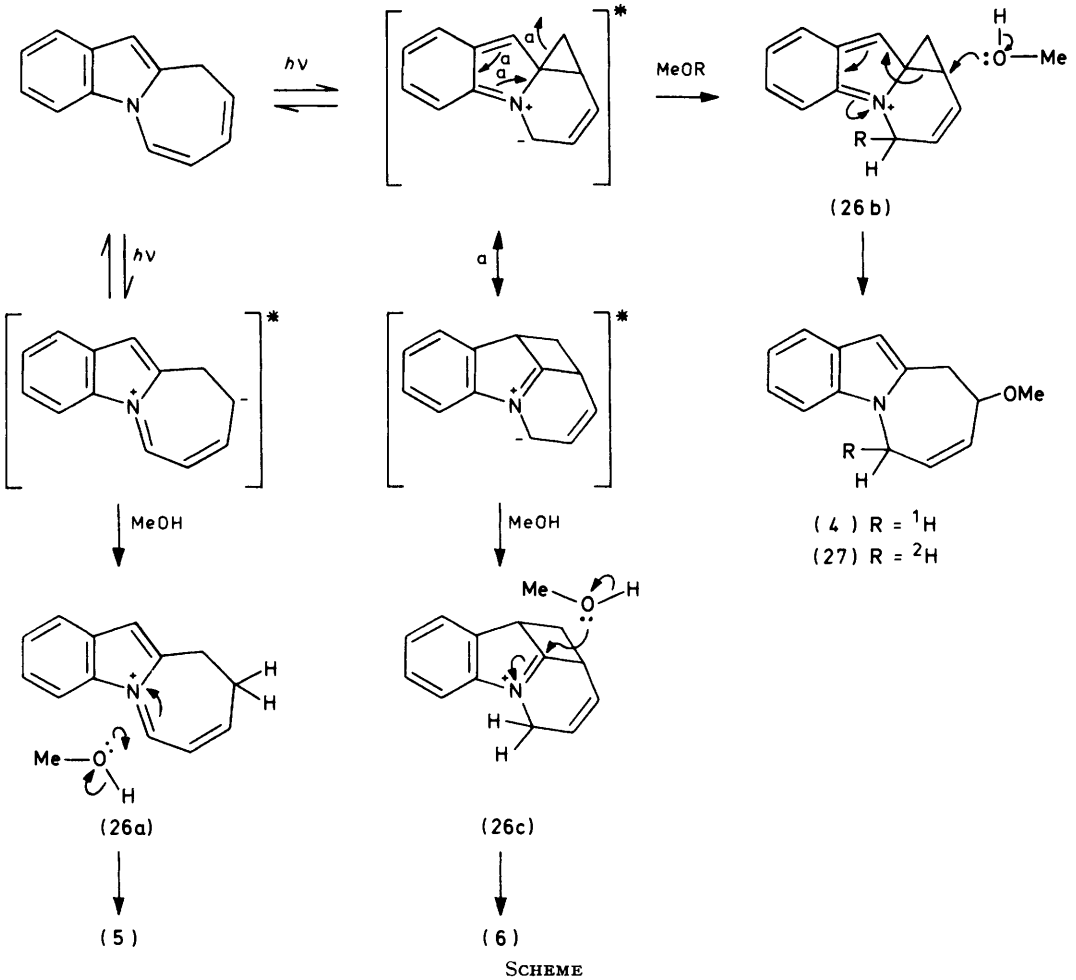
solid residue containing some polymer and some of the photodimer (3), but no alcohol addition products were identified. Irradiation in benzene gave only the photodimer and polymer, and irradiation in diethylamine or aqueous tetrahydrofuran gave no identifiable products.



(22)

DISCUSSION

We have made, as yet, no serious study of the photochemical mechanism of the addition of alcohols to azepinoindoles, but enough evidence is available for some discussion of the possible intermediates. Arylbutadienes have been found to produce a variety of products when photolysed in methanol, some of which result from the addition of an alcohol molecule.[16] The evidence seems to favour the excited singlet state as the source of addition products. The photochemistry of cycloheptadienes[13] and benzocycloheptadienes[14] has been thoroughly examined, but both of these systems characteristically undergo hydrogen shifts and electrocyclic reactions which are not observed in the case of the azepinoindoles. We assume that our reaction proceeds also from the excited singlet state; irradiation through quartz gave the same product mixture as the normal experiments with Pyrex, and no change in products was observed when acetophenone was added to the photolysis mixture. Crude estimates of the rate of disappearance of the maximum at 315 nm showed that there was little difference in the rate of removal of starting material when the solvent was changed, or when the azepinoindoles were varied. These observations could be accommodated by a rate-determining formation of the singlet excited state, which could then either be trapped by reactive alcohols (*e.g.* methanol or ethanol), or from dimers or polymers in the absence of reactive traps. The excited state is probably best represented by a dipolar species which can abstract a proton from methanol to form the positively charged species (26a or b). Attack on these carbonium ions by methanol, as shown in the Scheme, gives compounds of type (B) and (A) respec-



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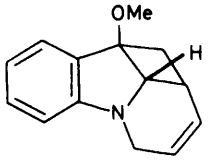
tively. Both species should, in principle, give rise to isomeric alkoxy-derivatives *via* attack at position 8, in the case of (26a), and position 7 for (26b), and it is notable that such derivatives [(18) or (22)] are formed when a methyl group confers increased stability on the appropriate carbonium ion. The dipolar excited species from which the cation (26b) arises is well set-up for a Wagner–Meerwein rearrangement to produce the precursor for the cyclobutanes, the carbonium ion (26c). An example of a Wagner–Meerwein rearrangement to an iminium ion is provided by Mariano [17] in the reaction of a cyanoalkene with a phenylpyrrolidinium salt. We have done a single labelling experiment to provide some evidence for the proposed mechanism, using methan[^{2}H]ol as solvent with the azepinoindole (1). Because of the smaller scale necessary we could not isolate products of type (B) or (C), but the compound of type (A), the azepinoindole (27), showed in its ^{1}H n.m.r. spectrum an integrated signal at δ 4.0 (6-H) of only one proton, thus confirming the position of protonation of the intermediate (26b). More surprising was the simplification of the signal at δ 5.25—5.45, due to 7-H, which was now revealed as a quartet of doublets [sixteen lines from compound (4)], with the apparently clean removal of one of the protons 6- or 6′-H. Inspection of a Dreiding model of the proposed intermediate (26b) reveals considerable obstruction to an approach from one direction, so the protonation may, in fact, be stereospecific. Another interesting feature of the spectrum of compound (27) is the partial exchange of 11-H, the signal at δ 6.3, which has an integration of <0.5 H; the opposite effect was observed for compound (7) in methanol, when an *increase* in the integration of 11-H was observed. We are investigating further this apparent photochemical substitution of the indole β-proton. A very small amount of a second product was fortuitously isolated from the chromatographic separation of the irradiation products of the azepinoindole (1) in methan[^{2}H]ol. While bearing a considerable resemblance to the spectrum of compound (6), the ^{1}H n.m.r. spectrum of this material is best interpreted as being due to the isomer (28) which could be derived, by a hydride shift, from the ion (26c). The



(28)

essential features in which compound (28) differs from compound (6) are all in the upfield section of the spectrum. A doublet (1 H) at δ 2.5 (9a-H) replaces the quartet (11-H) in compound (6). The pair of multiplets (10- and 10′-H) are closer together in compound (28), at δ 1.5 and 1.9, and the signal due to 9-H (unresolved multiplet) has moved upfield to δ 1.25 because the methoxy-group is now remote from position 9. Hence this product completes the series. With the sole exception of attack at 11-H in intermediate (26b), at least one compound has been obtained because of nucleophilic attack at each of the predicted sites of positive charge in the rearranged and unrearranged intermediates.

EXPERIMENTAL

All irradiation experiments were carried out with dilute solutions (1 g per 500 ml) using a Hanovia lamp (medium-pressure mercury) with a Pyrex sleeve, unless otherwise stated. The reaction mixtures were purified by chromatography on alumina columns (100 g per 1 g of starting material, Woelm activity IV) eluting with light petroleum (b.p. 60—80 °C); the crude products were evaporated onto 10 g of alumina and thus applied to the column. Further purification was achieved by p.l.c. (20 × 40-cm plates, Merck PF 254). ^{1}H N.m.r. spectra were obtained for solutions in deuteriochloroform unless otherwise stated. M.p.s were determined on a Köfler heated stage and are uncorrected.

10*H*-Azepino[1,2-*a*]indole (1), 11-methyl-10*H*-azepino-(1,2-*a*]indole (8), and [10,11-^{2}H$_2$]azepino[1,2-*a*]indole (7) were prepared by published procedures.[2,6]

2-(p-*Tolylmethyl*)*aniline*.—Prepared from 2-amino-4′-methylbenzophenone (15 g) by reduction with sodium in ethanol,[3] the *tolylmethylaniline* (13.5 g, 96%) had m.p. 64—66 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 85.25; H, 7.75; N, 6.95. $C_{14}H_{15}N$ requires C, 85.2; H, 7.65; N, 7.1%); δ 2.3 (3 H, s), 3.5 (2 H, br, NH_2), 3.9 (2 H, s), and 6.5—7.3 (8 H, m); *m/e* 197 (M^+) and 196 (100%).

1-*Azido*-2-(p-*tolylmethyl*)*benzene*.—Prepared as described [3] from the tolylmethylaniline (16.8 g), the *azido* compound (17.5 g, 92%) had m.p. 53—55 °C (from light petroleum, b.p. 40—60 °C) (Found: C, 75.1; H, 5.9; N, 19.0. $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.85; N, 18.8%); δ 2.3 (3 H, s), 3.9 (2 H, s), and 7.1 (8 H, m); $\nu_{max.}$ 2 120 cm^{-1}; *m/e* 223 (M^+).

8-*Methyl*-10H-*azepino*[1,2-a]*indole* (9)—Decomposition of 1-azido-2-(*p*-tolylmethyl)benzene (10 g) in trichlorobenzene at 190 °C (4 h) and work-up in the usual manner [3] gave, after chromatography on alumina, with light petroleum (b.p. 60—80 °C) as eluant, the *azepinoindole* (9) (4.5 g, 51%), m.p. 65—67 °C (light petroleum, b.p. 60—80 °C) (Found: C, 85.7; H, 6.75; N, 6.9. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.15%); δ 1.8 (3 H, s), 3.35 (2 H, d, *J* 6 Hz, 10-H), 5.6—5.8 (2 H, m), 6.1 (1 H, s, 11-H), and 7.0—7.8 (5 H, m); *m/e* 195 (M^+).

2-*Amino*-3′,5′-*dimethylbenzophenone*.—Prepared by the procedure of Lamchen and Wicken,[18] the *aminobenzophenone* (65%) had m.p. 65—67 °C (from ethanol) (Found: C, 80.35; H, 6.7; N, 6.4. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.6; N, 6.2%); $\nu_{max.}$(CHCl$_3$) 1 630 cm^{-1}; δ 2.3 (6 H, s), 6.0 (2 H, br, NH_2), 6.4—6.8 (2 H, m), and 7.0—7.6 (7 H, m); *m/e* 225 (M^+).

2-(3,5-*Xylylmethyl*)*aniline*.—Prepared from 2-amino-3′,5′-dimethylbenzophenone (15 g) by sodium and ethanol reduction,[3] the *xylylaniline* (14 g, 99%) was obtained as an oil (Found: C, 85.15; H, 8.2; N, 6.4. $C_{15}H_{17}N$ requires C, 85.25; H, 8.1; N, 6.6%); δ 2.2 (6 H, s), 3.4 (2 H, br, NH_2), 3.75 (2 H, s), and 6.5—7.2 (7 H, m).

1-*Azido*-2-(3,5-*xylylmethyl*)*benzene*.—Prepared from 2-(3,5-xylylmethyl)aniline (14 g) by diazotization and treatment with sodium azide,[4] the azide was purified by chromatography on alumina and obtained as an oil (15 g, 95%); $\nu_{max.}$ 2 100 cm^{-1}; δ 2.2 (6 H, s), 3.8 (2 H, s), 6.75 (3 H, br s),

and 7.0—7.3 (4 H, m); *m/e* 237 (M^+), 236, 208 (100%), and 194.

7,9-*Dimethyl*-10H-*azepino*[1,2-a]*indole* (10).—Decomposition of the azido-xylylmethylbenzene (10 g) in trichlorobenzene at 190 °C gave, after work-up, the *dimethylazepinoindole* (10) (4 g, 45%), m.p. 108—110 °C (light petroleum, b.p. 60—80 °C) (Found: C, 86.4; H, 7.35; N, 6.6. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); δ 2.0 (6 H, br s), 3.3 (2 H, s, 10-H), 5.6 (1 H, q, *J* 1 Hz), 6.1 (1 H, s, 11-H), and 7.0—7.8 (5 H, m).

Photolysis of 10-*Azepino*[1,2-a]*indole* (1).—(*a*) *In methanol.* After irradiation for 5 h, chromatography gave starting material (200 mg) followed by 1a,4,9b,10-*tetrahydro*-10-*methoxybenzo*[b]*cyclobuta*[hi]*indolizine* (6), b.p. 90—95 °C at 4×10^{-5} mmHg (bulb tube), m.p. 66—67 °C (*ca.* 100 mg, 9.5%) (Found: C, 78.9; H, 7.1; N, 6.6. $C_{14}H_{15}NO$ requires C, 78.8; H, 7.1; N, 6.55%); *m/e* 213 (17%, M^+), 198 (35, $M - CH_3$), 182 (35, $M - CH_3O$), 181 (100, $M - CH_3OH$), and 180 (100). The third fraction containing both compounds (6) and (5) was purified by p.l.c. (10% ethyl acetate in light petroleum, b.p. 60—80 °C, multiple runs); 6,9-*dihydro*-6-*methoxy*-10H-*azepino*[1,2-a]*indole* (5) had b.p. 120 °C at 2×10^{-3} mmHg (bulb tube) (50 mg, 5%) (Found: C, 78.7; H, 7.15; N, 6.95%); *m/e* 213 (M^+). The fourth compound obtained from the column was the *dimer* 16,16a,-16b,17-tetrahydrocyclobuta[1,2-*i*; 3,4-*i*]diazepino[1,2-*a*]-indole (30 mg, 3%) (3), m.p. >230 °C (benzene–cyclohexane) (Found: C, 85.6; H, 6.05; N, 7.35. $C_{26}H_{22}H_2$ requires C, 86.15; H, 6.1; N, 7.7%); δ (C_6D_6) 2.2 (1 H, m), 2.5—2.7 (3 H, m), 4.9 (1 H, dd, *J* 9 and 4 Hz), 6.3 (1 H, s), 6.5 (1 H, d, *J* 9 Hz), 7.1—7.2 (3 H, m), and 7.55—7.6 (3 H, m). The final compound eluted was 6,9-*dihydro*-9-*methoxy*-10H-*azepino*[1,2-a]*indole* (4), (0.25 g, 24% on unrecovered starting material) m.p. 96—97 °C (light petroleum, b.p. 60—80 °C) (Found: C, 78.75; H, 7.05; N, 6.45); *m/e* 214 (31%), 213 (100, M^+), 182 (47, $M - CH_3O$), 181 (80, $M - CH_3OH$), and 180 (47); $\lambda_{max.}$ 222, 276, 282, and 292 nm ($\log_{10}\varepsilon$ 4.55, 3.89, 3.89, —). Lengthening the time of irradiation led to an increased yield of compound (4) (up to 57% on one occasion).

(*b*) *In ethanol.* Evaporation of the solution after irradiation (7.5 h) gave a solid, some of which was insoluble in deuteriochloroform. Chromatography, as described above, gave the ethoxy-compounds (23)—(25). Products (24) and (25) were characterized by their mass (M^+ 227) and ^1H n.m.r. spectra only. The major product was 9-*ethoxy*-6,9-*dihydro*-10H-*azepino*[1,2-a]*indole* (23) (290 mg, 27%), b.p. 130 °C at 2×10^{-3} mmHg, m.p. 71—73 °C (Found: C, 79.05; H, 7.75; N, 6.1. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%); *m/e* 227.

(*c*) *In t-butyl alcohol–benzene.* Evaporation of this solution (6 h irradiation) yielded much insoluble solid. Chromatography gave starting material (*ca.* 150 mg) and the dimer (3) (300 mg) as the only identified products.

(*d*) *In methan*[^{2}H]*ol.* A solution of azepinoindole (1) (0.5 g) in methan[^{2}H]ol (180 ml) was irradiated for 5.5 h. Treatment as in (*a*) gave a small amount (*ca.* 6 mg) of a compound identified by spectroscopy as compound (28).

The [6-^{2}H]-6,9-dihydro-9-methoxyazepinoindole (27) had *m/e* 215 (20%), 214 (100, M^+), 213 (61), 183 (90), 182 (77), and 181 (54).

Irradiation of the 11-*Methylazepinoindole* (8) *in Methanol.*—From the azepinoindole (8) (0.9 g) in methanol (500 ml), after irradiation for 5.5 h, 550 mg of products were recovered from the column. In order of elution, the products were starting material (70 mg), the 1a,4,9b,10-tetrahydro-10-methoxy-9b-methylbenzo[*b*]cyclobuta[*hi*]indolizine (20) (50 mg, 5%), 6,9-dihydro-6-methoxy-11-methyl-10*H*-azepino[1,2-*a*]indole (16) (20 mg, 2%), and the 6,9-*dihydro*-9-*methoxy*-11-*methyl*-10H-*azepino*[1,2-a]*indole* (12), (0.35 g, 36%) m.p. 88—90 °C (from light petroleum) (Found: C, 79.4; H, 7.85; N, 6.0%).

Irradiation of the 8-*Methylazepinoindole* (9) *in Methanol.*—The azepinoindole (9) (1 g) gave, after chromatography, starting material (175 mg), 1a,4,9b,10-tetrahydro-10-methoxy-2-methylbenzo[*b*]cyclobuta[*hi*]indolizine (21) (*ca.* 100 mg, 11%), and 6,9-dihydro-6-methoxy-8-methyl-10*H*-azepino[1,2-*a*]indole (17) (*ca.* 100 mg, 11%); these compounds were characterized by their ^1H n.m.r. spectra and M^+ values. The fourth compound obtained from the column was 8,9-*dihydro*-8-*methoxy*-8-*methyl*-10H-*azepino*-[1,2-a]*indole* (18) (100 mg, 11%), b.p. 130 °C at 3×10^{-3} mmHg (bulb tube) (Found: C, 79.55; H, 7.55; N, 6.2. $C_{15}H_{17}NO$ requires C, 79.25; H, 7.55; N, 6.15%). The last compound eluted was 6,9-*dihydro*-9-*methoxy*-8-*methyl*-10H-*azepino*[1,2-a]*indole* (13) (110 mg, 12%), b.p. 140 °C at 5×10^{-3} mmHg (Found: C, 79.25; H, 7.5; N, 6.15%).

Irradiation of 7,9-*Dimethyl*-10H-*azepino*[1,2-a]*indole* (10) *in Methanol.*—The dimethylazepinoindole (10) (1 g) in methanol (500 ml) gave, after irradiation for 8 h and chromatography (alumina, 100 g), only a small quantity of starting material. The major fractions were mixtures of two compounds which were separated by p.l.c. (ethyl acetate–hexane, 1 : 9). The first band gave 6,9-*dihydro*-9-*methoxy*-7,9-*dimethyl*-10H-*azepino*[1,2-a]*indole* (14) (0.37 g, 32%), m.p. 96.5—97 °C (from light petroleum, b.p. 40—60 °C) (Found: C, 79.85; H, 8.15; N, 5.7. $C_{16}H_{19}NO$ requires C, 79.65; H, 7.95; N, 5.8%). The second band gave 6,7-*dihydro*-7-*methoxy*-7,9-*dimethyl*-10H-*azepino*[1,2-a]-*indole* (22) (0.3 g, 26%), m.p. 120—120.5 °C (from light petroleum, b.p. 40—60 °C) (Found: C, 79.55; H, 7.85; N, 5.65%).

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